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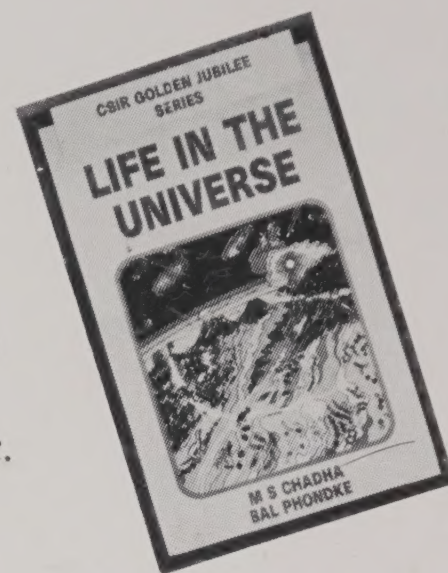
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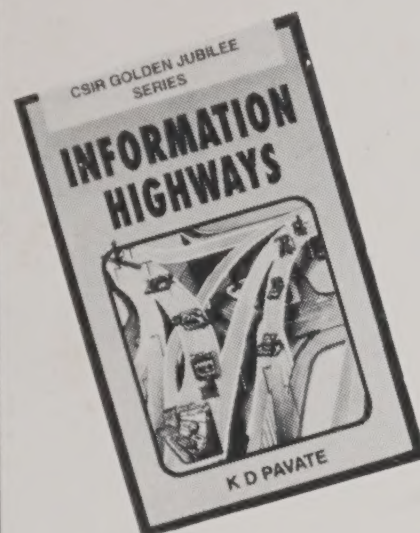
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## Paracetamol—An analysis of technologies for cleaner production

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Paracetamol, chemically known as acetaminophenone, N-(4-hydroxyphenyl) acetamide or 4-hydroxyacetanilide is an important and widely used antipyretic and analgesic agent, mainly due to its less side effects.

The major manufacturers of paracetamol world-over are:

- 1 Mallinckrodt, USA using p-nitrochlorobenzene route and having production capacity of 12,000 tpa.
- 2 Hoechst Celanese, USA using p-hydroxyacetophenone hydrazine route and having production capacity of 9,000 tpa.
- 3 Rhone Poulenc, USA and France using phenol route and having production capacity of 7,000 tpa.
- 4 McNeil, USA using nitrobenzene route.
- 5 Sterling Organics, UK using p-nitrochlorobenzene route and having production capacity of 3,000 tpa.

The present global demand of paracetamol is estimated at around 100,000 tpa.

In India, the paracetamol manufacture started in 1969 with a capacity of 10 tpa. At present, there are about 50 manufacturers in the country with production capacity of the order of 10,000 tpa, employing phenol and p-nitrochlorobenzene routes. 75% of the manufacturing units are located in Andhra Pradesh and Gujarat with 30% (approx) capacity each. There is a good export potential of paracetamol if cost of production could be reduced and the product meeting USP and BP standards could be produced.

For the paracetamol manufacture on commercial scale, the following four routes are used world-wide.

- 1 Phenol route
- 2 p-Nitrochlorobenzene route
- 3 Nitrobenzene route
- 4 p-Hydroxyacetophenone hydrazine route

Whereas the first three routes are employed for a long time, p-hydroxyacetophenone hydrazine route was employed in 1990 by Hoechst Celanese Corp., USA.

In the phenol route, phenol and sodium nitrite solution are cooled to less than 0°C and sulphuric acid is added slowly. The reaction is carried out at less than 0°C temperature. The reaction mass is filtered, p-nitrosophenol washed with water and reduced with sodium sulphide at 50°C. p-Aminophenol formed is filtered and purified with activated carbon in presence of hydrochloric acid.

In the p-nitrochlorobenzene route, p-nitrochlorobenzene is hydrolyzed with caustic soda at 160°C temperature and at around 6 kg/cm<sup>2</sup> pressure. The sodium salt of p-nitrophenol produced is reacted with sulphuric acid at around 40°C. p-nitrophenol is reduced in presence of iron and acetic acid at around 100°C. The reaction mass is filtered to remove iron sludge, the filtrate cooled to 15°C and filtered to get p-aminophenol.

In the nitrobenzene route, reduction of nitrobenzene is carried out either electrolytically or catalytically. In the electrolytic reduction, the reaction mass containing sulphuric acid salts of p-aminophenol and aniline is neutralised. Aniline is removed by distillation and the mass is treated with activated carbon to get pure p-aminophenol.

The details of p-hydroxyacetophenone hydrazine route are not available.

p-Aminophenol produced from any of the routes is then acetylated with acetic anhydride at 80°C and the mass is cooled and filtered to get crude paracetamol. The crude product is purified with activated carbon at 100°C, mass filtered and cooled to 10°C, sodium hydrosulphite added, mass centrifuged, dried and pulverized.



### Analysis of technologies being employed by Indian industry and recommendations for cleaner production

In the phenol route followed by some Indian industries, every ton of paracetamol results into 40,000 litres (approx) of effluent. The yield of paracetamol, based on phenol, obtained is around 60% (1.0t/t phenol). There is tremendous scope of reduction of effluent quantity and improvement of yields.

In the process being adopted, nitrosation is carried out by the reaction of phenol with sodium nitrite in presence of sulphuric acid in a wooden vat. Various chemicals used, per ton of paracetamol include 1050 kg (approx) phenol, 700 kg (approx) sulphuric acid, 1000 kg (approx) sodium nitrite and 170 kg (approx) sodium meta-bisulphite. The low reaction temperature (less than 0°C) is obtained by adding ice into the reaction mass. The reaction products are filtered and 15,000 lit effluent/ton of paracetamol is discarded. If alloy steel reactor is employed alongwith chilled brine plant, the effluent could be minimized at least by 10,000 lit/ton of paracetamol. With proper process control, the reaction could be optimized, loss of reactants and products minimized in the effluent, resulting into improved yields.

The reduction of nitrosophenol to p-aminophenol is carried out with the help of sodium sulphide, generated *in situ* by the reaction of sulphur with caustic soda, in acidic media and the reduced mass is neutralized with ammonium sulphate. The exothermic reaction is carried out at around 50°C. Various chemicals used, per ton of paracetamol include 900 kg (approx) sulphur, 1750 kg (approx) caustic lye, 1200 kg (approx) hydrochloric acid and 1050 kg (approx) ammonium sulphate. The reaction products are filtered and 8,000 lit effluent (approx)/ton of paracetamol is discarded. The p-aminophenol cake is then purified using activated charcoal in aqueous media and the filtrate generated is of the order of 10,000 lit/ton of paracetamol. If catalytic reduction is carried out with hydrogen and Pd/C catalyst, the effluent could be reduced by around 6,000 lit/ton of paracetamol. With better control of the reaction during catalytic hydrogenation and avoidance of various chemicals used at present, side reactions could be minimized. This would result into improved yield and purer p-aminophenol, requiring less activated carbon and water for its purification and thereby reducing the effluent by at least 6,000 lit/ton of paracetamol. Hydrogen transfer catalysis can offer all these advantages, without handling hydrogen gas. Electrochemical reduction of p-nitrosophenol can also result in less effluent and increased yields.

In the p-nitrochlorobenzene route, followed by many Indian industries, liquid effluent generated is 35,000 litres (approx) for every ton of paracetamol produced. The yield of paracetamol, based on p-nitrochlorobenzene is around 75% (0.75 t/t of pNCB). There is scope of reduction of effluent quantity and improvement of yields.

In the process being adopted, hydrolysis is carried out by the reaction of 9% caustic soda solution with p-nitrochlorobenzene. There is no automation for this exothermic reaction. 1335 kg (approx) p-nitrochlorobenzene and 800 kg (approx) caustic soda are used for every ton of paracetamol produced. The reaction mass is filtered and 8,000 litres of highly alkaline filtrate per ton of paracetamol is discarded. With suitable process control and proper design of the reactor, the yields could be optimized, resulting into lower requirement of inputs and generation of lower quantities of effluent.

The sodium salt of p-nitrophenol is then treated with concentrated sulphuric acid (850 kg per ton paracetamol) at 35-45°C. p-Nitrophenol is filtered and 2,000 litres of highly acidic filtrate per ton of paracetamol is discarded. With proper filtration and water wash, alkaline liquor trapped into sodium salt of p-nitrophenol could be minimized and thereby consumption of sulphuric acid for neutralization could be reduced. The dissolved salts content in the acidic effluent could also be reduced.

p-Nitrophenol is reduced with iron and acetic acid (530 kg and 53 kg per ton of paracetamol respectively) at 90-100°C temperature in wooden vat. The reaction temperature is raised by direct injection of steam. On completion of reduction, water is added to the reaction mass, iron sludge is removed by filtration and the filtrate is cooled to 15°C. p-Aminophenol is filtered and the filtrate (9000 lit/ton paracetamol) is collected. This filtrate, containing p-aminophenol could be re-used in the reduction step 4-5 times before being discharged as effluent. p-Aminophenol recovery from the effluent may be increased by further lowering its temperature, using some solvent or by salting out. This would improve the yields. Proper design of the reduction vessel alongwith optimum stirring speed should also result in the improvement of the yields. The iron sludge could be used for making iron oxide for red oxide primers. Catalytic hydrogenation<sup>1,2,3</sup> or electrolytic reduction<sup>4,5</sup> of p-nitrophenol is likely to give higher yields and avoid solid wastes. Hydrogen transfer catalysis is likely to give all these advantages, without handling hydrogen gas. Pure p-aminophenol is reported<sup>6</sup> to be prepared by adding more p-nitrophenol to the reaction mixture (if the reaction has gone to completion),



adjusting the pH between 5.0 and 6.5 and separating the p-nitrophenol phase (for re-use in reduction) and the p-aminophenol could be purified by giving treatment with carbon in aqueous hydrochloric acid solution and it could be stabilized by the addition of sodium sulphite.

The acetylation of p-aminophenol to crude paracetamol is carried out by the addition of 1000 kg (approx) acetic anhydride/ton of paracetamol. No attempt is made to control the temperature of this exothermic reaction. The temperature could increase to around 80°C. After cooling, crude paracetamol is filtered and 4,000 lit (approx) filtrate/ton of paracetamol is discarded. The crude paracetamol is given charcoal treatment and pure paracetamol is recrystallized in water, generating 8,000 lit/ton (approx) paracetamol effluent. The wet cake of paracetamol is centrifuged, dried and packed. The temperature control during acetylation may ensure complete acetylation of p-aminophenol and reduction of side products formation. The filtrate, after filtration of crude paracetamol, is dilute acetic acid solution containing unreacted p-aminophenol and paracetamol. Secondary acetylation may ensure that the conversion of p-aminophenol is complete. With solvent extraction, paracetamol could be recovered and dilute acetic acid could find some uses. The filtrate obtained after filtration of pure paracetamol could be re-used in the purification step 3-4 times before being discharged as effluent. Paracetamol could be recovered from this effluent by lowering its temperature or by solvent extraction or by salting out. This would improve the yields.

p-Aminophenol obtained as reduction product is also reported to be acetylated without isolation. Simultaneous reduction and acetylation<sup>7</sup> of p-nitrosophenol with hydrogen in presence of catalyst Pd/C, acetic acid and acetic anhydride can reduce number of process steps, increase the yields and minimize effluents to a large extent.

Modification<sup>8</sup> of acetylation process by pH control during acetylation with acetic anhydride and removal of water with the help of Dean-Stark water trap is reported to maximize the yields of paracetamol. Acetylation could also be modified<sup>9</sup> by dissolving p-aminophenol in acetic acid, treating the mixture with carbon and filtering; treating the filtrate with acetic anhydride and separating paracetamol, recycling the mother liquor after separation of paracetamol for use as solvent for dissolving p-aminophenol. In addition to reducing the effluent quantity, this process would increase the yields by minimizing loss of paracetamol in the acidic effluent.

During the purification of crude paracetamol by recrystallization from hot water, pH control to 6.5 by the addition of ammonia is reported<sup>10</sup> reduce the solubility of paracetamol in the acidic effluent, thereby increasing the yields.

Recrystallization in aqueous isopropanol<sup>11</sup> containing formamidine sulfinic acid and sodium bisulphite at 85-90°C for 15-20 minutes, cooling the mass to 10°C and filtering the mixture is reported to give better yields. This would help in reducing the effluent quantity and improving yields.

Purification of crude paracetamol may be attempted, without the addition of sodium bisulphite and sodium hydrosulphite, but by aerating<sup>12</sup> with hydrogen peroxide/peracetic acid, followed by charcoal treatment to remove iron oxides and oxidation by-products.

In addition to improvements suggested above in the production processes followed by the Indian Industry, using phenol and p-nitrochlorobenzene as the basic raw materials, the production of p-aminophenol by electrolytic reduction of nitrobenzene<sup>16</sup>, and coupling<sup>13</sup> of phenol with diazotized aniline in dilute sodium hydroxide, precipitating hydrozobenzene and hydrogenolyzing in methanol is also reported.

There is a mention of isomerization<sup>14</sup> of p-aminophenol in high yields to paracetamol in the presence of acetic acid or phosphoric acid. Paracetamol is reported<sup>15,16</sup> to have been prepared by Beckmann rearrangement of p-hydroxy-acetophenoxy oxine in the presence of thionyl chloride in potassium iodide-ethyl acetate solvent with 99.44% conversion.

It is reported<sup>17</sup> that the reaction of hydroquinone, acetamide and HZSM-5 zeolite gave 93.6% conversion of hydroquinone with 45.9 mole % of selectivity to paracetamol. The single step reaction of hydroquinone and ammonium acetate is reported<sup>18</sup> to give paracetamol with a selectivity of 75% on hydroquinone.

These new processes offer simplification in reaction steps and may be evaluated from techno-economic angle especially with respect to variable cost.

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## Process for pilot-production of seed and ascorbic acid fortified watermelon juice

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Studies were conducted on the compositional and sensory qualities of juice from two new watermelon cultivars, *H-23* and *Shipper* with and without added ascorbic acid. Bottled juice stored well over a period of six months under room temperature (12-40°C) and remained highly acceptable throughout. Improvement of inspid taste of fresh juice through sugar, acid adjustment was prerequisite to processing. Fortified juices showed losses of ascorbic acid during pasteurization, processing and storage. Study indicated the potential for commercial production and marketing of quality seed and vitaminized watermelon juice.

Watermelon botanically belongs to the family *Cucurbitaceae* and is a popular summer fruit. It is well known as short duration crop of high yield potentials growing on poor sandy soils. Watermelon is extensively cultivated in the beds of rivers, rivulets, drainages, sewerages and *choes*. It is also popular with the potato and other vegetable growers as short duration filler summer crop. Fruit pulp has attractive red colour, with sweet and refreshing taste. Since fruit harvesting coincides with the hot summer months of May-June, therefore, it is extensively consumed as fresh during the hot summer months. It also acts as appetiser, as it flushes out human system through excessive urination. Nutritionally, it is a rich source of minerals and lycopene, but poor in vitamin C<sup>1</sup>. Further, fruit rinde being thick, the fruit can be transported easily in loose packs over long distances. It can also be retained for couple of days at the retailers shop under prevailing high room temperatures before its final disposal and consumption.

High-yielding varieties of watermelon have been successfully developed and released for commercial cultivation by the breeders. Popularity of high-yielding varieties among growers coupled with improved cultural practices has resulted in shortage of seed and also its availability at high cost. Mechanization of the process for simultaneous recovery of seed and juice is explained for the benefit of seed producers and processors. Commercial seed production is carried out only by limited growers. Therefore, mechanized recovery of seed can prove a boon to the commercial seed producers owing to the high cost of manual seed production and scarcity of labour. Mechanically separated seed yields are higher with better seed quality.

In this paper, suitability of two new varieties of watermelon, i.e. *H-23* and *Shipper* was studied for production of bottled juice as by-product; seed being the main product. Furthermore, watermelon is a poor source of vitamin C. Therefore, in order to increase its nutritional and therapeutic value, study was extended to pilot-plant production of ascorbic acid fortified watermelon juice.

### Materials and Methods

Two hundred kg fruit of each watermelon cultivar of *H-23* and *Shipper* were harvested from the University Vegetable Farm and processed into seed and juice. Melons were washed, halved and their pulps along with seeds were scooped out by pressing the fruit halves against the revolving burrs of mechanically operated Burring machine with precaution not to scrap out the white portion of the rinde, which otherwise imparted starchy taste. Resulting mixture of pulp and seed was separated by passing it through the superfine pulper (Raylons) fitted with 0.3 mm dia sieve. Brix/acid ratio of juice was adjusted and it was heated immediately to 85°C in a steam jacketed kettle till the surface scum (foam) disappeared. After filtration, the hot juice was packed in 650 ml white beer bottles followed by their corking and processing in boiling water for 45 min in steam connected boiling water tanks. Processed bottles were cooled down immediately to room temperature in the same tanks by circulating cold water and stored at room temperature (12-40°C). Viable seeds were separated from the immature ones and fibrous portion by flowing away with running water in tanks. The viable seeds being heavier settled down easily. They were recovered on the sieve



(12 mesh) by filtration, washed well and sun-dried on aluminium (3' × 2') trays. The seeds were retained for sowing during the next kharief season and tested for their germination capacity prior to sowing.

In order to improve the inspid quality of fresh juice, sugar : acid ratio was adjusted prior to pasteurization. Fresh juice being poor source of vitamin C, was fortified with ascorbic acid at varied levels (Table 2) at the pasteurization temperature of 85°C followed by processing and storage in 650 ml bottles over 1/2 year under ambient temperature conditions (12-40°C).

Fresh and vitaminized juices were analyzed for : TSS with hand refractometer, acidity by titration against standardized 0.1N NaOH, pH with Elico pH meter, total and reducing sugars by Lane and Eynon method and ascorbic acid by titration against standardized dye following the methods detailed by AOAC<sup>2</sup>. Sensory analysis of the stored product was conducted by trained panel assigning scores : 4 for excellent, 3 for good, 2 for fair and 1 for poor; for individual sensory attributes of colour, aroma, taste, body and consistency.

### Results and Discussion

Composition of fresh juice shows that there were not appreciable differences in physico-chemical characteristics of juices from both the cultivars (Table 1). Fresh juice was low in TSS (8.4° brix) and poor in acidity (0.07%) which was also reflected by high pH (5.33). Therefore, juice as such was found unsuitable for further processing. Sugar : acid ratio was adjusted prior to filling to improve upon the sensory quality of the juice. Although levels of total sugars in fresh juice were found similar in both the varieties, yet *H-23* contained higher percentage of reducing sugars from *Shipper*. Both the varieties were also found poor in vitamin C containing less than 4 mg per cent. Since watermelon juice is a poor source of ascorbic acid therefore, the possibility of its fortification with ascorbic acid was explored.

Incorporation of additives prior to bottling resulted in corresponding increase in soluble solids as presented in Table 2. Although, ascorbic acid was added at the pasteurization temperature, yet some part of it was lost during cooling operation. The vitamin, being highly thermolabile in nature, is expected to be lost rapidly when added at such elevated temperatures. Approximately ten per cent of the added ascorbic acid was lost during the entire processing operation in *H-23* (Table 3) while higher losses were observed for *Shipper*. In general, per cent retention of ascorbic acid increased with the elevated levels of the additive, although it declined beyond the limit of 80 mg per cent. Stability of ascorbic acid in the

Table 1—Composition of fresh juice of *H-23* and *Shipper* watermelons

Composition	<i>H-23</i>	<i>Shipper</i>	Mean
TSS as °Brix	8.6	8.2	8.4
Acidity as citric acid %	0.08	0.05	0.07
pH	5.25	5.4	5.33
Reducing sugars as glucose %	5.0	3.68	4.34
Total sugars as glucose %	6.8	6.2	6.5
Ascorbic acid as mg %	3.6	4.3	3.95

Table 2—Effect of additives and pasteurization on juice composition

Added ascorbic acid mg %	Retained ascorbic acid mg %	pH	Acidity citric acid %	TSS °Brix	Reducing sugars %	Total sugars %
<i>H-23</i>						
0	0.5	4.05	0.27	11.6	5.43	9.4
20	18.7	4.05	0.27	11.6	5.43	9.4
40	38.4	4.0	0.28	11.6	5.43	9.4
60	57.6	4.0	0.28	11.6	5.45	9.3
80	76.0	4.0	0.29	11.6	5.45	9.3
100	94.0	4.05	0.29	11.6	5.45	9.3
<i>Shipper</i>						
0	0.7	4.1	0.28	12.0	4.5	9.3
20	18.7	4.1	0.28	12.0	4.5	9.3
40	38.4	4.1	0.28	12.0	4.55	9.3
60	57.6	4.05	0.29	12.0	4.55	9.4
80	75.0	4.1	0.29	12.0	4.55	9.4
100	93.6	4.1	0.29	12.0	4.55	9.3

Table 3—Ascorbic acid retention of fortified watermelon juice during storage at room temperature (12-40°C)

Added ascorbic acid mg %	% retention of ascorbic acid after storage period, weeks					
	<i>H-23</i>			<i>Shipper</i>		
	Initial	13	26	Initial	13	26
20	89.6	64.5	44.5	85.9	60.25	39.0
40	89.4	78.3	52.9	83.2	75.13	62.5
60	90.4	74.7	66.6	89.0	96.4	69.8
80	94.4	78.1	68.0	91.0	76.5	70.0
100	87.9	80.8	69.9	83.8	75.95	70.9
Mean	90.3	75.2	58.4	86.6	72.85	62.4

fortified watermelon juice stored under high room temperature (12-40°C) showed decline in the vitamin during storage. Decline was more pronounced after 3 months of storage in case of *H-23* where the ascorbic acid losses were of the tune of 13 per cent during the first three months which increased to 35 per cent at the end of six months. *Shipper* showed



almost uniform loss of vitamin throughout the storage period, being 28 per cent after 6 months. These losses could be substantially minimized if the product had been stored under refrigerated temperature. Study revealed that added ascorbic acid remained fairly stable during the first three months.

Other compositional changes occurred during storage are presented in Table 4. There were negligible changes in these physico-chemical characteristics. Solids, total sugars and acidity remained constant. However, there was marginal increase in reducing sugars which was attributable to the hydrolysis of non-reducing sugars occurring

Table 4—Effect of variety and storage period on composition of watermelon juice

Variety	Added ascorbic acid mg %	TSS °Brix	Reducing sugars %	Total sugars %	pH	Acidity citric acid %
Initial						
<i>H-23</i>	0	11.6	5.68	9.4	4.2	0.28
	20	11.6	5.68	9.4	4.2	0.28
	40	11.6	5.68	9.4	4.2	0.28
	60	11.6	5.68	9.3	4.2	0.28
	80	11.6	5.7	9.3	4.2	0.29
	100	11.6	5.7	9.3	4.2	0.29
<i>Shiipper</i>	0	11.8	5.4	9.3	4.2	0.28
	20	11.8	5.3	9.3	4.2	0.28
	40	11.8	5.4	9.3	4.2	0.29
	60	11.8	5.4	9.4	4.2	0.28
	80	11.8	5.3	9.4	4.1	0.28
	100	11.8	5.3	9.3	4.1	0.28
13 weeks storage at room temperature (12-40°C)						
<i>H-23</i>	0	11.8	6.2	9.2	4.2	0.27
	20	11.6	6.2	9.3	4.15	0.28
	40	11.6	6.1	9.2	4.15	0.29
	60	11.4	6.1	9.3	4.2	0.28
	80	11.4	6.0	9.3	4.2	0.28
	100	11.6	6.1	9.3	4.1	0.28
<i>Shiipper</i>	0	11.8	5.9	9.4	9.1	0.28
	20	12.0	5.85	9.3	4.1	0.30
	40	11.8	5.9	9.2	4.1	0.28
	60	11.6	6.0	9.2	4.2	0.29
	80	11.8	5.0	9.3	4.2	0.28
	100	11.8	5.6	9.3	4.1	0.28
26 weeks storage at room temperature (12-40°C)						
<i>H-23</i>	0	11.6	6.2	9.5	4.15	0.29
	20	11.8	6.3	9.1	4.1	0.27
	40	11.6	6.1	9.3	4.1	0.28
	60	11.4	6.0	9.3	4.2	0.28
	80	11.2	6.0	9.2	4.1	0.29
	100	11.4	6.0	9.2	4.1	0.29
<i>Shiipper</i>	0	11.4	6.0	9.1	4.2	0.28
	20	11.8	5.9	9.2	4.15	0.28
	40	11.6	5.9	9.4	4.1	0.29
	60	11.8	6.1	9.3	4.2	0.28
	80	11.8	6.2	9.3	4.2	0.28
	100	11.8	4.1	9.2	4.2	0.29

Table 5—Sensory score of watermelon juice stored under room temperature conditions (12-40°C)

Character	Storage period, weeks					
	Initial	13 <i>H-23</i>	26	Initial	13 <i>Shiipper</i>	26
Colour	4.0	4.0	4.0	4.0	4.0	4.0
Aroma	3.5	3.25	3.15	3.75	3.6	3.5
Taste	3.5	3.5	3.25	3.75	3.75	3.5
Body and consistency	3.25	3.25	3.2	3.5	3.5	3.3

slowly in the presence of acids upon prolonged storage.

Sensory evaluation studies conducted for stored bottled product revealed that juice remained highly acceptable even after half year of storage under high ambient temperature (12-40°C). Colour score remained excellent throughout (Table 5). However, there was marginal decline in aroma and taste score.

There were not appreciable differences in seed germination (93-95%) prepared by both the methods, viz. mechanical separation or manual extraction. However, manual extraction was found costlier. It also gave 17 per cent less seed recovery. Pulp had to be discarded. Therefore, mechanical extraction where both seed and juice can be recovered at a reasonable cost seems to have promising future for its adoption as such or with some modifications by the seed producers at their farm levels.

It was concluded that bottled watermelon juice could be stored satisfactorily for more than half year under high room temperature conditions. Adjustment of sugar : acid ratio of the fresh juice was prerequisite to processing. Plain juice as such was of inferior inspid taste. Pilot-plant study conducted on the production of watermelon juice indicated that both the varieties under investigation were equally good for processing into juice. Nutritional quality of the juice can be further improved by addition of ascorbic acid. Keeping in view the processing losses and daily requirements of the ascorbic acid, a reasonable level of 60 mg per cent of the added ascorbic acid is suggested. Conclusively, pilot-scale production of vitaminized bottled juice envisages for its popularization especially for anemic and jaundice patients.

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## Microcrystalline cellulose from "Pieceup" waste

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A method for preparing Microcrystalline Cellulose (MCC) from "Pieceup" waste of rayon mill has been described. This method does not require high energy and chemical inputs compared to MCC prepared from other sources. The characteristics are compared with those of other commercial MCCs. The product confirms to the ISI standards.

Microcrystalline Cellulose is mainly used in foods, cosmetics and drugs. It is a depolymerised and disintegrated cellulose product. MCC is generally prepared from high- $\alpha$ -pulp by controlled hydrolysis with dilute mineral acids. The product is subjected to shear whereby cellulose microcrystals are released from the main fibre structure.

Battista and co-workers prepared MCC from wood pulp and cotton linters<sup>1-3</sup>. Baichwal *et al.* prepared MCC from cotton cellulose and evaluated as tablet excipient<sup>4</sup>. Jacopian and others prepared MCC from saw dust<sup>5</sup>. Newsprint waste was recycled into MCC by Nagavi & Mithal<sup>6-8</sup> who also studied characteristics of MCC and its uses in drug dosage forms. Anand and Chawala prepared MCC from bleached cotton hosiery waste<sup>9</sup>. Abdullah ABM, prepared MCC from jute<sup>10</sup>. The main raw material for the production of MCC is purified high- $\alpha$ -cellulose.

### Materials and Method

In viscose rayon manufacturing units at the time of starting spinning machines or fibre tow breakdown, leaves in to unstretched fused filament tow is called "Pieceup". It is a partially regenerated cellulose rich in  $\alpha$  contents but does not possess fibre properties and goes as a waste.

The present work aims at investigations on the preparation of MCC from white {Bright} pieceup waste available at viscose rayon manufacturing industries. Analysis of fresh pieceup waste shows presence of cellulose, cellulosexanthate (coagulated viscose), sodium sulphate and by-products of carbon-di-sulphide etc. Typical analysis of pieceup waste is given in Table 1.

### Pre-treatments

The above analysis shows that beside cellulose, pieceup contains lot of impurities, therefore pretreatment is necessary. First of all fresh pieceup tow was cut into small pieces and impregnated in boiling acidic water 1:20 solid liquor ratio for about 2 hours. This treatment removes sulphides ( $\text{CS}_2$  and its by-products) and dissolves out inorganic salts like sodium sulphate and zinc sulphate. Then it was washed with hot water 3-4 times till free from sulphate ions. Finally it is dried in air.

### Preparation of Hydrocellulose

Treated cuttings were then subjected to acid hydrolysis at 100-104 deg.C. boiling under reflux with dilute hydrochloric acid. After required time the reaction mixture was filtered and the acid collected as the filtrate. The acid hydrolysed cellulose (hydrocellulose or depolymerised cellulose) was washed to remove acid. The acid recovered from the first hydrolysis was used in subsequent experiments after making up losses. The recycling of acid was repeated four times. The hydro-cellulose was washed

Table 1—Proximate chemical analysis of pieceup waste

Property	Pieceup Waste as such	After Pre-treatment
Moisture(%)	50 to 60	10-15
Cellulose (% on O.D. basis)	30 to 40	85-90
Lignin	Negligible	Negligible
Total Sulphides (%)	4-5	Negligible
Total Sulphate (%) (as $\text{Na}_2\text{SO}_4$ )	5-7	Negligible
Acidity (%)	1-2	Neutral



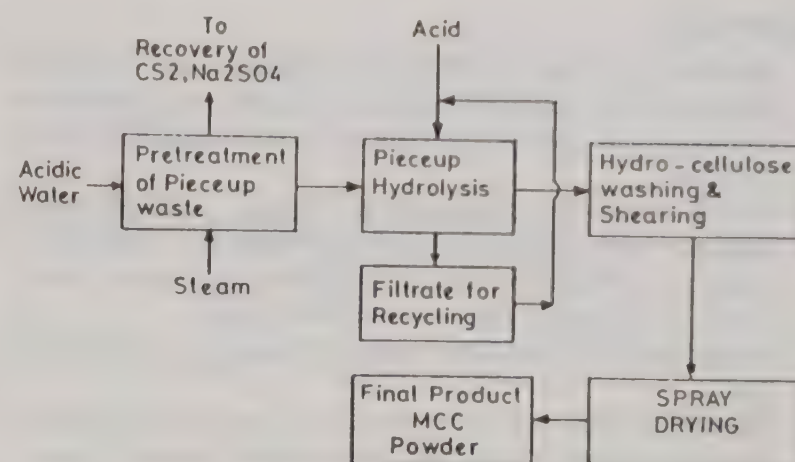
with water till free from acid and finally washed with small quantity of alcohol to remove traces of water. The hydro-cellulose product showed a slight decrease in brightness with the reuse of the acid. Results are indicated in Table 2.

### Preparation of Microcrystals

The hydrocellulose was then subjected to mechanical separation of microcrystals. This is usually done by a mechanical shearing to the hydro-cellulose in an aqueous medium for half an hour using blender. The mechanically sheared product was then dried. The properties of the end product depends upon the type of raw material, solid-liquor ratio, type of shearing, time and the method of drying.

It was observed that the product on drying in an oven at 100 deg.C. resulted in a change in colour. Therefore it is recommended to dry the product at low temperature, preferably through spray dryer.

The MCC prepared by this method is white odourless, insoluble and dispersible in water. It swells slightly in alkali. It is insoluble and resistant to dilute acids and insoluble in most of the organic solvents. Characteristics of MCC is given in Table 3. Snow-white MCC could be obtained by bleaching the pieceup before hydrolysis.



Flow diagram for the manufacture of MCC from pieceup

Table 2—Conditions of acid hydrolysis

Reaction Variable	Hydrolysis Reaction No.			
	I	II	III	IV
Wt of Pieceup cutting (g)	100	100	100	100
Solid : Liquor ratio	1:14	1:14	1:14	1:14
Recoverable acid (%)	90	89	88	86
Reducing sugars [as Glucose] in recovered acid solution (%)	0.7	1.2	1.5	1.9
Yield of hydro-Cellulose (%)	78	77	75	74

Table 3—Characteristics of MCC

Characteristic	Requirements as per ISI <sup>11,12</sup>	Avicel CL 611	MCC <sup>13</sup> CPIL	MCC Pieceup
Moisture (% by Mass)	Max. 5	3-5	5.0	5.0
Sulphated ash (% by Mass O.D. Basis)	Max. 0.2	—	0.24	0.2
Bulk Density (g/ml)	0.25 to 0.35	0.30 to 0.48	0.25 to 0.35	0.35 to 0.55
pH Value	5.5 to 7.0	6.8	5.5 to 7.0	6.0 to 7.0
Matter Soluble in Water % by Mass(O.D. basis)	0.2 Max.	—	0.2 Max.	0.2
Arsenic as As (mg/kg)	Max. 2	—	2 Max.	Passes test
Total heavy metals (as per) (mg/kg)max.	15	—	15	-do-
Whiteness	White to Offwhite	—	White	Off-White
Odour	Odourless	—	Odourless	Odourless

IS 9598-1980 & IS 2088-1983.  
MCC-CPIL-Cellulose Products of India Limited.

### Conclusion

This is an inexpensive method of preparing MCC using pieceup waste of viscose rayon mill. This method does not require high grade costly pulp as essential raw-material. Treated pieceup waste is by itself a pure form of cellulose. The process does not require high energy and chemicals input to isolate pure cellulose like other sources.

The quantity of the end product thus obtained is insufficient to meet the demand of large consumers as compared to other cellulosic products. Therefore it could be preferable to make use of pieceup by a small scale manufacturing unit associated with the viscose rayon mill.

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## Cotton stalk particle boards—A timber substitute

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Particle boards are timber substitutes which find wide applications in the building, furniture, and automobile industries. The preparation and characteristics of particle boards from cotton stalks, such as the effect of particle size and resin content (urea formaldehyde) on the properties of particle board is dealt with. The quantity of resin for board preparation has also been optimised to ensure properties in conformity with BIS specifications. With increase in resin content the density and modulus of rupture of the board were found to increase with a corresponding decrease in water absorption (WA) and thickness.

Particle board industry was started in India in a big way only in the fifties. However, this industry could not profitably sustain itself in Indian environment, the reasons being that among other things, the timber-based raw material is scarce, and the tropical climatic conditions are not so conducive for the use of particle boards. It is expected that by the turn of the century wood will be a rare and one of the most sought-after commodities not only in India but the world over in view of the rate at which forest and forest resources are depleting. Hence, there is a need for finding substitutes for wood in many of the wood-based Industries. Some advanced countries have undertaken crash programmes to utilise agrowastes for conserving material resources of timber. Particle board is one such material which is a wood-based panel<sup>1</sup> and provides a surface greater in length and corss section than wood. The board prepared by using lignocellulosic wastes can substitute timber. According to the estimate of FAO, the annual requirement of industrial wood in India is about 12 million tonnes whereas the supply is only 5.7 million tonnes<sup>2</sup>. The present position regarding production of particle boards and fibre boards which are timber substitutes in the country is given in Table 1 along with plywood production.

India is one of the leading cotton growing countries in the world. The total area under cotton cultivation is about 8.0 million hectares, which generates cotton stalks to the extent of about 15.0 million tonnes annually. The cotton stalk which is used as fuel by the rural masses to a limited extent is later disposed of generally by burning in the fields itself in order to avoid any build-up of pests. Central Institute for Research on Cotton Technology has done pioneering work on utilisation of cotton salks for the production

Table 1—Production of particle board and fibre board in India  
in 1000 m<sup>3</sup>

Year	Ply	PB	FB
1970	128	11	34
1980	200	28	20
1985	364	38	48
1986	351	41	49
1987	470	45	63

of pulp and paper<sup>3</sup>, for growing edible mushrooms<sup>4</sup>, in preparation of cellulose derivatives, and for kraft paper and corrugated boxes. Cotton stalk can also be used for the production of various types of particle boards having good strength properties and composite material to substitute building materials in flooring, partitioning, ceiling and in production of furniture articles.

Depending upon the quantity of lignocellulosic materials used, particle boards can be classified into three types, for specific end uses as mentioned blow.

- Low density board (up to 400 kgm<sup>-3</sup>) for thermal and acoustic insulation applications.
- Medium density board (500-800 kgm<sup>-3</sup>) for building and furniture Industry.
- High density boards (900 kgm<sup>-1</sup> and above) for furniture and in specialised purposes such as jigs and other fixtures and in general engineering industries<sup>5</sup>.

In this paper, the effect of particle size and resin content on the physical and mechanical properties of particle boards has been discussed.



## Materials and Methods

Cotton stalk was collected from fields after harvest and was dried in the sun for facilitating removal of leaves, boll rinds, undeveloped bolls, etc. When the moisture content of the stalk was about 15 per cent, the stalk was chopped on the chaff cutter to about 1.5 to 2 cm chips. These chips were ground on a beater type mill and sieved to get particles of 8 mesh to 50 mesh size. Particles finer than 50 mesh were not used for the experiment, as they have the disadvantage of high resin absorption. The pulverised stalk was analysed as per TAAPI standard test methods<sup>6</sup> (Table 2) for different chemical constituents like cellulose content, per cent hot water solubles, lignin percentage, etc.

## Experimental Procedures

*Effect of particle size on board properties*—The quality of the board is dependent upon uniform mixing of the binder. As the resin is the most expensive ingredient in board making and the amount of resin required per unit volume of the board depends on the size and shape of particles, the selection of optimum sized particle becomes very imperative.

In order to determine this factor, the cotton stalk chips are powdered in a beater type mill and the powdered product sieved through sieves of different mesh sizes. Series of experiments were conducted using different sized particles to prepare boards using same quantity of resin for all the experiments.

Different sieved fraction were labelled according to Table 3.

200 g each of the sieve fraction was taken and mixed with a definite quantity (10%) of resin (urea formaldehyde). The mat of resin treated particles was formed by putting it in a wooden frame and then pressed at 165°C temp under 35 kg/cm<sup>2</sup> pressure on the board for 4.5 minutes. The boards were tested for physical properties such as density, thickness, moisture content and mechanical properties like modulus of rupture (MOR) water absorption and

thickness swelling and the results are given in Table 4.

*Effect of resin content on properties of particle board*—Resin content is considered as an important variable that influences the physico-mechanical properties of particle board<sup>7</sup>. After establishing the optimum particle size of cotton stalks, next important parameter was to establish the optimum requirement of resin for board preparation to meet the BIS specification laid for the board.

To study this aspect the mixture of C and D (−10 M + 15 M) was divided into seven equal parts each weighing about 200 g. The resin was sprayed on each lot of cotton stalk particles in the proportion ranging from 3 to 15 per cent on the weight of raw material. Then the resin blended material was dried and boards were prepared as mentioned earlier. The boards were cooled, kept overnight for equilibrium with atmospheric conditions and then cut to required sizes for carrying out different tests for assessing the quality. These boards were tested for different properties according to BIS specifications<sup>8</sup> and the results are given in Table 5.

Table 2—Proximate analysis\* of cotton stalks

	Percentage
Moisture content	9.2
Hot water solubles	12.3
1% Alkali solubles	23.8
Ash	6.9
Alcohol benzene extractives	5.4
Holocellulose	77.6
Lignin	27.2

\*Analysis for each constituent is done separately.

Table 3—Different fractions of cotton stalk particles

A.	Particle size retained over BS 4 mesh sieve (+4 M)
B.	" BS 10 mesh sieve (−4 M + 10 M)
C.	" BS 25 mesh sieve (−10 M + 25 M)
D.	" BS 50 mesh sieve (−25 M + 50 M)
E.	Passed through 50 mesh sieve (−50 M)

Table 4—Properties of boards prepared from different particle size of cotton stalks

Board No.	Particle size	Thickness mm	Density gm/cc	Moisture content of board (%)	WA %	MOR (kg/cm <sup>2</sup> )	Thickness swelling (%)
1.	A (+4 M)	9.8	0.82	7.0	76	106	58
2.	B (−4 M + 10 M)	9.3	0.88	7.1	72	115.2	55.5
3.	C (−10 M + 25 M)	8.4	0.92	7.2	67	120.5	44
4.	D (−25 M + 50 M)	7.8	0.96	6.8	54	152.4	19
5.	E (−50 M)	6.2	0.98	6.7	32	96.2	16

Pressure — 35 kg/cm<sup>2</sup>, Resin — 10%, Temp: 165°C, Time — 4.5 min.



## Results and Discussion

The proximate analysis of cotton stalk shows that it contains good amount of lignin and cellulose, viz. 27 per cent and 78 per cent respectively; hence it can be good raw material for making boards, pulp and paper.

The properties of particle board, prepared by using cotton stalk particles of different mesh sizes have been given in Table 4. The results showed that the particle size labelled as D, i.e. particles passed through 25 mesh BS sieve and retained over 50 mesh BS sieve exhibited good properties. However, the mixture of particles passed through 10 mesh and retained over 50 mesh (C & D) BS were considered better since these in subsequent trials yielded high strength property. The strength had reduced for the boards made with still finer particles passed through 50 mesh possibly due to less surface area.

It is seen from Table 5 that increase in resin content affects all physical and mechanical properties favourably. With an increase in resin content from 3 per cent to 15 per cent the density is increased from 0.72 to 0.88 and Modulus of rupture from 75.0 kg/cm<sup>2</sup> to 190.0 kg/cm<sup>2</sup> whereas the water absorption of board decreased from 57 per cent to 22 per cent and the thickness swelling due to surface absorption from 22 per cent to 6 per cent. Overall a resin content of 8 per cent was not only found to be optimum for board preparation, to meet the BIS specification but also gave better properties than those made from conventional raw material.

## Conclusion

From the above study it may be concluded that the optimum particle size, geometry and shape of the particles constitute a very important factor to be considered in board preparation. Cotton stalk particles passing through 10 mesh and retaining over 50 mesh are proved to be good for board preparation. Resin content influences the physical and mechanical properties of the board appreciably. With increase in

Table 5—Properties of the particle boards prepared from cotton stalks with urea formaldehyde as binder

% Resin	Thickness mm	Density gm/cc	MOR kg/cm <sup>2</sup>	WA %	% Swelling due to surface absorption
0	7.1	0.70	62.0	77	28
3	7.4	0.72	75.0	57	22
5	7.6	0.76	95.0	42	18
8	8.0	0.78	126.5	33	12
10	8.2	0.82	136.1	31	10
12	8.4	0.84	142.0	28	9
13.5	8.5	0.84	178.0	25	8
15	8.9	0.88	190.0	22	6

Pressure — 35 kg/cm<sup>2</sup>, Temp. 165°C, Time — 4.5 min.

resin content the density and MOR, increase while WA decreases. A resin content of 8 per cent is optimal at which the board pass the requirements of BIS.

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## Combined RO-ion-exchange process for high purity water

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Generally for boiler feed, water of high purity is required although water of low grade is used for low pressure general purpose boilers. The objective of combined technique of reverse osmosis (RO) and ion-exchange is to reduce the cost of process water by reducing the load on ion-exchange columns by removing major portion of the dissolved solids by RO. Cost comparison for different quality feed waters by RO, ion-exchange and combined technique has been discussed. Quality of product water at different recovery levels by RO for different feeds shows that as the recovery of product water increases its quality decreases. Results also show that at higher total dissolved solids (TDS) of feed water combined technique is more economical than either of the techniques and a break-even point has been arrived at.

Water is a biological necessity for all forms of plant and animal life. For human beings, the need for water extends to various fields. This tasteless, colourless and odourless liquid, exists everywhere in nature. It is also an almost universal solvent and practically all substances are soluble in it to some extent. Therefore chemically pure water is extremely rare and difficult to obtain.

Generally for boiler feed, water of high purity is required although water of low grade is used for low pressure general purpose boilers. Thus the quality of water required for boiler feed purpose, is dependent on boiler design, its operating pressure and purpose for which it is being used<sup>1</sup>.

Reverse osmosis technique developed basically for desalination of brackish and sea water has been found useful for many other applications where good quality of water is required. Since reverse osmosis technique cannot give completely desalinated water, the technique as it is cannot suffice the need of high pressure boiler water. Hence it should be supplemented with some other method to remove remaining dissolved substances.

The most suitable method envisaged is ion-exchange technique and is considered feasible for obtaining feed water for high pressure boilers.

### Experimental Procedure

The different quality well waters are processed by RO unit. The effluent is recycled to obtain desired recovery level of feed water. Feed, product and concentrate streams were analysed for their ionic content. Permeate is then passed through regenerated Zeokarb and Deacidite FFIP exchangers.

Water was collected in reservoir till the conductivity of product water was less than 7 to 8 mhos. Volume of the water collected before break-through was measured and analysed for its pH, conductivity and silica content.

### Results and Discussion

Quality of product water with respect to recovery and membrane rejection at different recovery levels for different feed waters is different.

It is seen that salt rejection at different recovery levels has remained more or less constant to about  $\pm 0.5$  per cent. This indicates that ionic rejection by the membrane is remaining same for different brine concentrations. The curve of salt rejection at different recovery levels, indicates that as percentage recovery increases (though membrane rejection remains constant) overall rejection based on original feed concentration decreases. This is due to the fact that with the recovery of product water the feed concentration increases which results in an increase in the TDS of the product water. These data are very much useful in finding out the percentage recovery level for a desired quality product water from a given feed.

The product water from RO plant possesses good clarity and is very low in dissolved solids and silica. It can, in fact be used directly in some industries.

It can be seen that silica content of product water obtained by only ion-exchange technique is more than by using combined technique of RO and ion-exchange. The TDS of product water obtained by ion-exchange treatment is found to be in the range of 17 to 20 ppm which is more than the required limit



Table 1—Cost of water treatment by only ion-exchange and RO + ion-exchange<sup>2</sup>

Well water No.	% Recovery by RO	TDS ppm	TDS as CaCO <sub>3</sub> ppm	Silica content ppm	Chemicals required for 5000 L water treatment				Chemical cost Rs	Total RO + chemicals Rs	Saving Rs
					NaOH in kg	Rs	HCl in kg	Rs			
1	*	370	546	14	2.72	40.8	10.7	5.35	46.15	46.15	—
	50	33	66	3	0.375	5.625	1.47	0.735	6.36	131.36	—
	75	46	92	4	0.555	8.325	1.54	6.77	14.095	133.09	—
2	*	612	974	23	6.00	90.0	23.6	11.8	101.8	101.8	—
	50	84	120	6	0.75	11.25	2.95	1.475	12.725	137.22	—
	75	108	158	8	1.0	15.0	3.94	1.97	16.97	16.97	1 142.00
3	*	926	1170	48	7.7	115.0	33.0	16.5	131.5	131.5	—
	50	110	204	14	1.36	20.4	5.36	2.68	23.08	148.8	—
	75	175	248	17	1.66	24.9	6.56	3.28	28.18	153.18	—
4	*	1139	1302	8.5	8.84	132.6	24.7	12.35	144.95	144.95	—
	50	262	130	2	0.88	13.2	3.07	1.535	14.735	139.73	5.22
	75	296	204	3	1.25	18.75	4.96	2.48	21.23	146.23	—
5	*	1810	2186	57	16.63	249.45	65.6	32.8	282.25	282.25	—
	50	260	300	1.6	2.14	32.1	8.44	4.22	36.32	161.32	120.93
	75	308	340	21.5	2.4	36.0	9.44	4.72	40.72	165.72	116.53

\*Feed water

Foot Note: 1. a, Silica removal only by IE depends on the nature of the silica and it can be as high as 60%; b, Silica content by combined technique is brought down to 1-2 ppm.

Foot Note: 2. TDS by RO + IE is brought down to less than 5 ppm while by IE alone it is in the range of 17-20 ppm.

set for boiler operation while the combined technique gives the product water containing 4 to 7 ppm TDS.

The cost of chemicals required for processing 5000 litres of different types of water containing varying amounts of TDS expressed as ppm of calcium carbonate is presented graphically as also in Table 1. It is evident from the figure that the cost of chemicals is increasing linearly. This indicates that the cost is directly proportional to the TDS of water. The cost of water produced by the combined technique of RO and ion-exchange at 50 and 75 per cent recovery level also follows similar trend, except that in the case of '50 per cent recovery' the initial value is less to some extent than in the case of '75 per cent recovery'. It is seen from the Fig. 1 that below 1250 and 1180 ppm TDS (75 and 50 per cent recovery level) ion-exchange technique is more economical than the combined technique<sup>2</sup>. But as TDS increases in the feed water, per cent saving in chemical cost slowly increases for 50 and 75 per cent recovery. Moreover, it is also observed that for 1800 ppm TDS saving in chemical cost is to the extent of 40 to 45 per cent.

### Conclusion

1. There is a saving of about 30 to 50 per cent in the cost of treatment.
2. Ion-exchange demineralization unit when used to

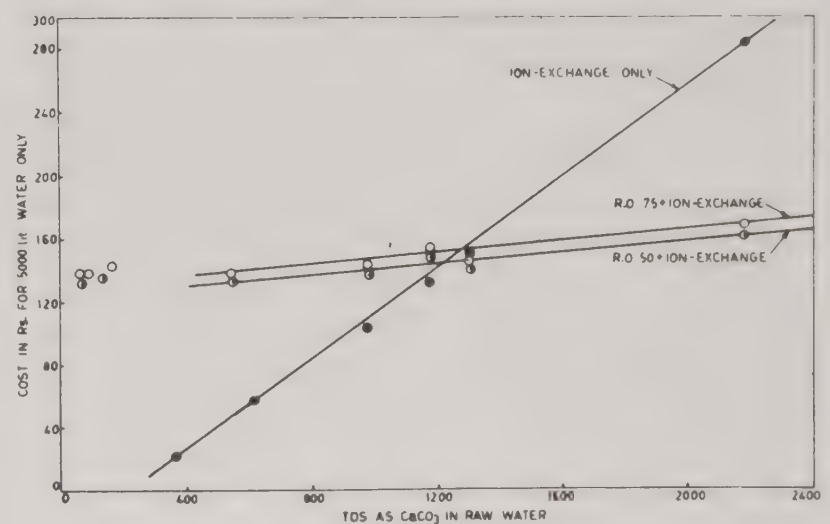


Fig. 1—Cost comparison of ion-exchange and RO

demineralization of the RO product water, produces 5 to 8 times more quantity with good quality between each regeneration cycle.

3. The use of RO before the ion-exchange operation essentially eliminates the fouling of the resin bed, by organic, microbiological, iron, manganese and silica impurities of the water.

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## Evaluation of oil and seed meal of three exotic collections of *Vernonia galamensis* (Cass) Less

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Three exotic collections of *Vernonia galamensis* (Cass) Less introduced earlier were evaluated for physico-chemical attributes of oil, fatty acid profile and composition of defatted seed meal. Accession 211347 had higher oil and vernolic acid content while accessions 212470 and 212471 showed a better fatty acid composition.

*Vernonia galamensis* (Cass) Less has been recently recognized as an important industrial crop<sup>1</sup>. This annual herb native to semi-arid regions of Africa is cultivated as an industrial crop in Zimbabwe and has undergone promising agronomic trials in Kenya, Tanzania and Pakistan<sup>1,2</sup>. The seeds of this plant contain about 40 per cent of a triglyceride oil of which about 76 per cent is comprised of an epoxy acid commonly known as vernolic (cis-12,13-epoxy-cis-9-octadecenoic) acid thus making the species an excellent source of naturally epoxidized triglyceride oil with both current and potential application in industry<sup>3-5</sup>. AEGIS (Agricultural Ecological and Geographical Information System) computer system on the basis of rainfall and temperature published a map including 19,000 location of the world where *V. galamensis* is adopted as new crop<sup>6</sup>. Recently some exotic and indigenous collections of *Vernonia* were introduced at the Regional Research Laboratory, Jammu-Tawi (North-West India), and evaluated for growth performance and yield potential<sup>7-11</sup>. In continuation of the above work the present study records physico-chemical property of oil, its fatty acid profile and composition of defatted seed meal of three exotic collections of *V. galamensis*.

### Materials and Methods

Authentic seed samples of 5.0 gm each of the three accessions were procured through the courtesy of NBPGR, New Delhi. Seeds were sown in first week of September in raised nursery beds and later on 15 October 1989 at four leaf stage were transplanted in fields beds at 60 × 60 cms row-to-row and 70 × 70 cms plant-to-plant and raised to maturity under normal daylight conditions. Seeds collection from 10 randomly selected plants at maturity from each

accession were cleaned and used for estimation of oil and its vernolic acid composition according to the method of Harris *et al.*<sup>12</sup> and averaged. Physico-chemical attributes of oil and composition of defatted seed meal was ascertained in triplicate from each accession by standard AOAC procedures<sup>13</sup> and averaged. Fatty acid composition was determined in triplicate oil samples randomly picked from each accession by standard GLC procedure on Pye Unichem 204 Series gas chromatograph with a flame ionization detector using 2 m × 3/10 ID SS column packed with 20 per cent DEGS on Chromosorb W (60-80 mesh) at 190°C isothermally. Peaks were confirmed by log plots C' retention time versus carbon numbers.

### Results and Discussion

The three accessions showed a marginal difference in oil content and its vernolic acid composition (Table 1). A higher oil content of 35.4 per cent and 78.4 per cent vernolic acid was recorded in accession 211347 followed by 32.6 per cent oil and 73.2 per cent vernolic acid in accession 212471. The physico-chemical attributes of oil were comparable in the three collections. However, the levels of essential fatty acids (oleic acid and linoleic acid) were relatively higher than saturated fatty acids (palmitic and stearic acid). The fatty acid composition of accessions under study was similar to the earlier finding<sup>5,14,24</sup> with the exception that the content of linoleic acid and oleic acid was slightly higher. On the contrary stearic acid composition was very low and ranged between 0.27-0.99 per cent as compared to 2.23 per cent reported earlier. The protein fibre and ash content in the seed meal was less than those in the earlier reports<sup>5</sup>.



Table 1—Evaluation of oil seed meal of three accessions of *Vernonia galamensis*

(a) physico-chemical attributes	accessions		
	211347	212470	212471
oil %	35.4	30.8	32.6
Sp. gravity	0.95	0.92	0.94
saponification value	188.0	186.4	187.6
iodine value	99.5	98.3	98.0
unsaponifiable matter	3.6	3.0	2.5
(b) fatty acid composition			
lauric acid	0.27	1.13	0.38
myristic acid	0.30	1.05	0.28
palmitic acid	2.18	3.83	3.72
stearic acid	0.27	0.99	0.73
oleic acid	5.47	6.53	6.71
linoleic acid	12.4	14.3	14.1
arachidic acid	0.62	1.13	0.84
vernolic acid	78.4	71.0	73.2
(c) composition of defatted seed meal			
moisture %	8.40	7.80	8.00
residual oil %	0.50	0.46	0.40
protein %	40.8	38.4	34.6
ash %	5.60	7.80	6.40
source of material	accessions introduced from		
	1. 211347 Min of Agr, USA		
	2. 212470 Chiredi, Res St, Zimb.		
	3. 212471 Ag Res Cent Beltsville, USA		

The potential commercial applications of *V. galamensis* seed oil are well documented in recent literature<sup>2,3,5,14</sup>. The oil has attracted great attention leading to both academic and industrial research activities<sup>15,16</sup> with a variety of interests such as reactive diluents for high solid based paints, toughened epoxy resins, lubricants and lubricant additives, adhesives, insecticides and insecticide repellents, crop oil concentrates and formulations of carriers for slow release of insecticides and pesticides<sup>17</sup>. It is hoped that this list will further grow as industry becomes increasingly aware of the properties, uses and availability of vernonia oil. A procedure<sup>18</sup> for extraction of oil from *V. galamensis* seeds at pilot plant scale has been standardized and oil has been proved to be a good natural source for synthesis of aliphatic dibasic acids<sup>19,20</sup> which serves

as reactive diluents for high solid-based paints, Ayorinde *et al.*<sup>22</sup> reported enzymatic synthesis of 1,3-divernoloyl glycerol from vernonia seed oil. The seed oil has also been used for synthesis of epoxy secondary amides<sup>23</sup> thus further enhancing the usage of vernonia seed oil.

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## Development of heat-treated light-weight terracotta bodies containing low-grade talc

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Additives not only improves the required properties in final product like dimensional accuracy, water absorption, mechanical strength, etc. but also contributes to energy conservation (being used as fluxes), insulating properties, act as filler and extender. Keeping this in view, a study on the influence of a additive (low grade talc) on red clay was carried out to develop heat treated light weight bodies by measuring dry and fired properties, when added progressively. The influence of low grade talc additions to plastic red clay is progressively more significant with increase in firing temperatures from 950° to 1100°C. The impurities present in talc mainly free lime behaves as an inert material at low temperatures (< 950°C) and then as an opening agent at higher temperatures up to 1050°C and thus reducing the fired shrinkage to appreciable extent.

The traditional terracotta bodies are generally made by using plastic red clay with additives like sand, rice husk ash, red clay grog, etc. The ratio of components mainly depends upon physico-chemical properties of clay, the impurities present in clay and the desired properties of finished product.

Although the red clays are hydrated aluminosilicates and mainly consist of kaolinitic mineral but are always associated with various types of impurities like free quartz, feldspar, calcite, haematite, rutile, etc. in addition of montmorillonitic and illitic minerals. The presence of these impurities severely affect the firing range of product, dimensional accuracy and other fired properties. Due to all these shortcomings the red clays alone are not used to produce any specialised terracotta product, and some additives are always incorporated to the mixes of red clays. The addition of additives broadly control the various properties of body mix like; dry and fired shrinkages, firing range of body mix, pore formation, mechanical properties, viz, strength, toughness & modulus, and finally, thermal shock resistance of material.

Keeping this in view, a study was undertaken for findings the influence of low grade talc as additive on a plastic red clay by firing at different test temperatures (900° to 1100°C). The object of the work is to develop heat treated light weight terracotta product or specialised items with required porosity, mechanical strength and of better dimensional accuracy from red clay.

### Materials

The soapstone, taken for studying the effect, have the composition as furnished in Table 1.

Quarse potter's clay is cheaply and abundantly available at village Quarse of Khurja Tahsil. The colour of clay is grey and slacking in nature. The chemical and rational analysis of the clay is furnished in Table 1. The mineralogical composition, as ascertained from rational analysis, indicates that the

Table 1—Chemical assay and rational analysis of Quarse clay and talc

Constituents	Quarse clay	Low grade talc
Chemical analysis		
SiO <sub>2</sub>	63.83	37.13
TiO <sub>2</sub>	0.98	0.15
Al <sub>2</sub> O <sub>3</sub>	15.31	2.65
Fe <sub>2</sub> O <sub>3</sub>	4.97	1.21
CaO	2.47	22.36
MgO	1.48	14.87
Na <sub>2</sub> O	2.73	1.35
K <sub>2</sub> O	3.02	0.30
L.O.I	5.22	20.30
Rational analysis		
Feldspar	40.52	
Kaolin	18.87	
Quartz	27.28	
Calcite	4.36	
Magnesite	3.08	
Haematite	4.92	
Rutile	0.97	
Hydrated magnesium silicate	—	60.31
Fee lime (CaCO <sub>3</sub> )	—	39.63



clay contains low kaolinitic mineral along with substantial quantity of quartz and feldspathic impurities. The wet sieve analysis is also furnished in Table 2. The details of physico-chemical properties of this clay have been published separately.

### Experimental Conditions

The Quarse clay and low grade talc mixtures as furnished in Table 3 were studied.

The Quarse clay was powdered and then mixed with low grade talc as per proportions mentioned in Table 3. The water was then added to make it plastic mass and kept for ageing for 3 days.

The rods of 20 mm in diameter and the length around 150 mm were extruded in a de-airing pug mill at a evacuated pressure of 0.8 in Hg. The rods were dried slowly under natural condition and fired in an electric kiln to different test temperatures.

The free or mechanically held water present in the bodies as extruded was computed on the dry basis from the weights taken immediately after forming and after drying to constant weight at 110°C. The linear shrinkage of the body mixes were measured with a vernier calliper, using reference marks pressed on the rods at 100 mm just after extrusion. Water absorption, apparent volume porosity and bulk density were determined by weighing specimens before and after keeping them in boiling water for 2 hrs and after suspending in water.

Modulus of rupture was measured by centre loading method at 50 mm span.

M.O.E. was measured by elasto-sonic instrument (ELASTO SONIC 1000 manufactured by M/s Nirmachal Engineering (P) Ltd, Bangalore).

### Results and Discussion

**Workability**—Optimum workability of these plastic mixes, prepared by extrusion was judged by hand feel method rather than by some mechanical means. The difference in workability was not notable in all the mixes.

**Plastic and dry properties**—The plastic and dry properties are furnished in Table 4. The high value of Atterberg's number, water of plasticity and dry linear shrinkage of non-talc batch may be due to presence of some portion of bentonitic/montmorillonite mineral as well as higher proportion of finer particles below 2  $\mu$ . On addition of talc, the decrease in Atterberg's no. and dry linear shrinkage are analogous to the fact that addition of non-plastic materials in place of plastic material reduces plasticity and shrinkage, but in QT<sub>3</sub> batch the relationship between water of plasticity and dry linear shrinkage have distributed might be due to

reaction of free lime (present in higher proportion in low grade talc) with water, which has affected the cumulative properties of water of plasticity.

The highest value of dry M O R (60.71 Kg/cm<sup>2</sup>) of QT<sub>1</sub> batch may be due to typical particle density at a ratio of 60 per cent coarse and 40 per cent fine particles.

**Fired linear shrinkage**—The fired linear shrinkage of mixes are furnished in Table 5.

The results show that there is no appreciable shrinkage up to 900°C in non-talc batch (QC) which may be inferred due to low-clayed content (18.87%) of Quarse clay and non-start of pyro-chemical reaction in the mix. But in talc mixes (QT<sub>1</sub>, QT<sub>2</sub> &

Table 2—Wet sieve analysis of Quarse clay

Wet sieve analysis fraction	% by wt
+ 60 mesh	1.01
– 60 + 100 mesh	3.92
– 100 + 200 mesh	9.87
– 200 + 325 mesh	8.60
Retention over 75 micron (200 mesh)	14.80
Retention over 45 micron (325 mesh)	23.80
Particle finer than 1 micron	36.5
Particle finer than 2 micron	45.0
Particle finer than 10 micron	60.5

Table 3—Composition of mixes

Constituents	Compositin of mixes			
	QC	AT	QT <sub>2</sub>	QT <sub>3</sub>
Quarse clay	100	90	80	70
Low grade talc	—	10	20	30

Table 4—Dry and plastic properties of mixes

Properties	Mixes			
	QC	QT <sub>1</sub>	QT <sub>2</sub>	QT <sub>3</sub>
Atterberg's number	18	12	11	9
Water of plasticity (% by wt)	29.8	25.6	24.6	26.8
Dry linear shrinkage (%)	6.93	6.66	6.55	6.52
Dry modulus of rupture (Kg./cm <sup>2</sup> )	51.0	60.7	56.3	55.5
Particles coarser than 2 micron (%)	55	59.1	62.5	65.4
Particles finer than 2 micron (%)	45	40.9	37.5	34.6

Table 5—Fired linear shrinkage of mixes

Mixes	% Fired linear shrinkage at firing temperatures (°C)				
	900	950	1000	1050	1100
QC	0.71	1.94	2.9	6.72	7.56
QT <sub>1</sub>	0.45	0.49	0.54	1.56	3.90
QT <sub>2</sub>	0.30	0.33	0.36	0.71	2.35
QT <sub>3</sub>	0.30	0.37	0.48	0.91	2.15



QT<sub>3</sub>), there is no appreciable shrinkage up to 1000°C. It can thus be thought the talc does not react (or hardly react) with the clays in this temperature range and act as opening material, reducing the shrinkage very sharply at all test temperatures from 1000° to 1100°C on increasing the proportion of low grade talc from 10 to 30 per cent.

The results also show that in non-talc batch (QC) the firing shrinkage increases very sharply with the rise of temperature, but it is stabilised by addition of talc to improve the dimensional uniformity and firing range up to ~ 1050°C. It can further be thought that the sharp rise in shrinkage after ~ 1050°C might be due to the calcium oxide (developed from the decomposition of free lime present as impurities in low grade talc), which develops a vitreous phase by combination with silica and alumina to form calcium silicoaluminates. But at 1100°C all the batches showed over firing effect, which may partly due to low alumina content.

*Apparent volume porosity*—The results are furnished in Table 6. The apparent volume porosity decreases with the rise of test temperatures but very sharply from 950°C in case of non-talc batch QC but the addition of low grade talc stabilises the apparent volume porosity (25 to 28%) from 900° to 1050°C. The sudden decrease of apparent volume porosity at 1100°C in all the samples indicates the nearly complete vitrification.

*Per cent water absorption*—The results are furnished in Table 7. The water absorption varies from 0.33 to 15.28 per cent in non-talc batch QC. But this variation is reduced with increasing amount of low grade talc for the same firing range, i.e. 900° to 1100°C. It is also expected that the respective values and the variation should depend primarily on nature of clay than the clay/talc ratio to lesser extent.

*Bulk density*—The results are furnished in Table 8. The results show that the bulk density increases with gradual increase of firing temperatures. But at the firing temperatures of 900 and 950°C, the bulk density increases with addition of low grade talc (~ 10%) than decrease with further addition of low grade talc, while at higher firing temperatures (above 1000°C) the bulk density decreases with gradual addition of low grade talc. This again confirms that there is no pyro-chemical reaction in the mixes up to temperature of around 950°C especially in clay-talc batches and the consolidation of material is, essentially, the consequence of crystallisation and solid state transformation.

*Modulus of rupture*—The results are furnished in Table 9. In case of non-talc batch (QC) the fractural strength increases sharply with gradual increase in

firing temperatures. But in case of clay-talc mixes (QT<sub>1</sub>, QT<sub>2</sub> & QT<sub>3</sub>) the fractural strength first decreases and then increases, as analogous to behaviour of bulk density. The variation in fractural strength in clay-talc mixes mostly depends upon firing temperatures, nature of clay and talc but to lesser extent on clay/talc ratio.

*Modulus of elasticity*—The results are furnished in Table 10. It is evident from the results that the modulus of elasticity increases very sharply in non-talc batch (QC) but at lower rate in clay-talc batches as analogous to other fired properties.

The M O E was also measured after repeated thermal shocks (at 600°C + water quenching) on the specimens fired at different test temperatures. The values are furnished in Table 11.

Specimens fired at higher test temperature show more percentage loss in MOE than those of specimens fired at low temperature.

Table 6—Apparent volume porosity of mixes

Mixes	% App. volume porosity at firing temperatures (°C)				
	900	950	1000	1050	1100
QC	27.79	25.31	17.69	8.11	0.68
QT <sub>1</sub>	25.91	25.74	25.85	25.16	13.97
QT <sub>2</sub>	25.27	26.35	27.66	26.10	19.26
QT <sub>3</sub>	26.87	27.26	29.32	29.97	23.33

Table 7—Water absorption of mixes

Mixes	% Water absorption at firing temperatures (°C)				
	900	950	1000	1050	1100
QC	15.28	13.52	10.13	3.61	0.33
QT <sub>1</sub>	13.81	13.77	13.71	12.97	6.50
QT <sub>2</sub>	13.73	14.97	15.06	14.65	9.57
QT <sub>3</sub>	15.16	15.41	16.62	16.91	12.25

Table 8—Bulk density of mixes

Mixes	Bulk density (gm/cc.) at firing temperatures (°C)				
	900	950	1000	1050	1100
QC	1.82	1.87	1.92	2.24	2.34
QT <sub>1</sub>	1.87	1.88	1.89	1.93	2.14
QT <sub>2</sub>	1.84	1.84	1.84	1.84	2.01
QT <sub>3</sub>	1.77	1.77	1.77	1.77	1.87

Table 9—Modulus of rupture of mixes

Mixes	Modulus of rupture (Kg/cm <sup>2</sup> ) at firing temperatures (°C)				
	900	950	1000	1050	1100
QC	146	160	194	288	305
QT <sub>1</sub>	124	114	128	156	271
QT <sub>2</sub>	133	127	130	142	205
QT <sub>3</sub>	132	118	131	148	193



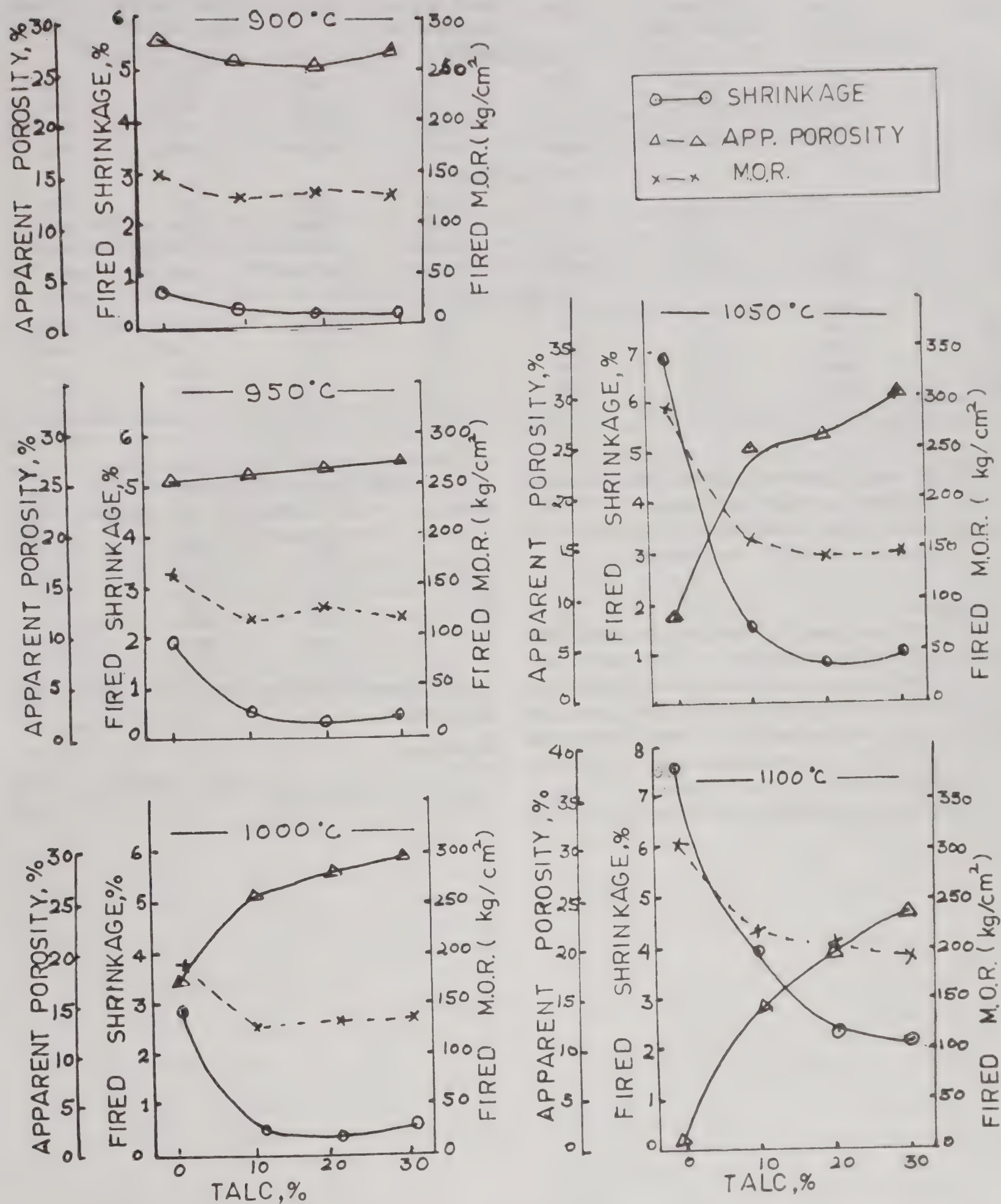


Fig. 1—Fired properties of clay-talc mixes



Table 11—Effect of talc on M O E after repeated thermal shocks (at 600°C + water quenching) on samples fired at different temperatures

Mixes	Original M.O.E	MOE after 1st thermal shock	% Loss	MOE after 2nd thermal shock	% Loss	MOE after 3rd thermal shock	% Loss
Fired at 900°C							
QC	19.34	13.939	27.92	11.697	39.55	9.45	51.14
QT <sub>1</sub>	20.44	13.962	31.7	11.556	43.49	8.566	58.1
QT <sub>2</sub>	21.04	14.211	32.45	12.30	41.53	11.83	43.78
QT <sub>3</sub>	21.86	14.326	34.46	9.8	55.16	6.89	68.5
Fired at 1000°C							
QC	31.143	15.96	48.74	12.78	58.96	7.6	75.6
QT <sub>1</sub>	20.97	13.08	37.62	10.68	49.07	8.56	59.17
QT <sub>2</sub>	19.80	11.83	40.20	10.46	45.45	8.90	55.05
QT <sub>3</sub>	18.92	10.233	45.53	8.45	55.33	6.0	68.28
Fired at 1100°C							
QC	53.91	12.23	77.31	8.42	84.38	6.0	88.87
QT <sub>1</sub>	34.390	19.95	41.98	8.82	74.35	8.203	76.67
QT <sub>2</sub>	28.487	23.93	15.97	8.43	70.40	6.86	75.91
QT <sub>3</sub>	30.822	13.75	55.38	6.98	77.35	5.4	82.48

The QC batch (non-talc) shows better thermal shock resistive at test temperature of 900°C in comparison of talc batches but it is reverse on the test temperature of 1000°C and above.

### Conclusion

It is evident from the data of dry and fired properties that the addition of low grade talc improves the dimensional accuracy and vitrification range as well as keeps the required fired properties (Fig. 1) within a tolerance limit for a wide firing range of around 100°C to manufacture heat treated light weight products. It may also be inferred as a case to manufacture any specialised item with required fired

Table 10—Modulus of elasticity of mixes

Mixes	M.O.E (GPa) at diff. firing temperatures (°C)		
	900	1000	1100
QC	19.34	31.14	53.9
QT <sub>1</sub>	20.44	21.00	34.4
QT <sub>2</sub>	21.04	19.8	28.5
QT <sub>3</sub>	21.85	18.9	28.5

properties under limiting values and having a wide firing range.

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## Evaluation methods for protective clothing against chemicals

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Evaluation by permeation assembly, closed chamber HD (Distilled sulphur mustard) drop, static diffusion and TNO GC methods was carried out for permeable and impermeable protective clothings for protective potential against CW agents and for quality control. Multiple HD test was employed in the case of the samples which gave a very high sulphur mustard breakthrough times. Indigenously developed protective clothings were found to be comparable to their foreign counterparts in their performance.

Potentially hazardous chemicals are liable to affect human skin adversely. Leather garments, plastic rain coats and rubber covers can offer some degree of protection. After a massive use of sulphur mustard during First World War, efforts were made to develop effective protective clothing. In past, this type of clothing was based on decomposition principle, where the protective outfit was impregnated with certain chemicals capable of decomposing or decontaminating the adsorbed toxicants. Presently, permeable protective clothing is obtained either by coating charcoal over non-woven fabric or by immobilizing carbon in polyurethane. Recent trends include the development of protective clothing from activated charcoal cloth. However, impermeable protective clothing was developed using either synthetic material like polyurethane or by coating nylon fabric with butyl rubber on one side and neoprene on the other.

It is emphasized that evaluation methods form an essential part in finding out the protective potential of permeable and impermeable fabric materials. It will be worth mentioning that these tests should include the methods for quality control and confidence building. Test facilities were established for this purpose based on international standards. The indigenously developed protective clothing was evaluated vis-à-vis its foreign counterpart for quality control and comparison of protective potential. Also, the indigenous clothing was evaluated for chemical protections only.

### Experimental Procedure

Permeation assembly<sup>1</sup>, closed chamber HD drop test method<sup>2</sup> and TNO GC method<sup>3</sup> were employed to evaluate the permeable protective clothing while static diffusion test method<sup>4</sup> was used for the evaluation

of impermeable protective clothing. Sulphur mustard was used as the challenge chemical for evaluating and monitoring the protective potential of protective clothing although other organic toxic chemicals have also been used for this purpose<sup>5-7</sup>.

#### 1. Permeation Method<sup>1</sup>

(a) *Test assembly*—On a brass plate 50 mm dia. is placed a disc of 38 mm dia. of white cotton drill retained by a flanged brass ring (the spacer ring) 1 mm thick, 53 mm internal dia. at the flange, with a hole 19 mm dia. in the centre. The purpose of the flange is to aid location on the brass plate. On the white cotton drill exposed in the 19 mm hole drops of mustard totalling 12  $\mu$ L are dispensed from a micrometer syringe. This system provides a standard concentration of mustard vapour in the space above the cotton drill. The spacer ring is covered with a 50 mm dia. glass disc, and the whole assembly is kept in a fume cupboard maintained at  $20 \pm 1^\circ\text{C}$  for 30 minutes. 2 discs of 50 mm dia. were cut from the specimen cloth and these were temporarily placed with the charcoal sides facing each other on the glass disc. For cloth samples subjected to the accelerated ageing procedure it is necessary to add a disc of paper impregnated with sodium carbonate, and on the top of these test piece discs was laid a disc of detector paper, 38 mm dia. After the 30 min period for temperature and vapour equilibration, the glass disc is removed, the test piece and detector paper discs are laid on the spacer ring, detector paper uppermost, and are retained in place by means of a flanged locating ring 1 mm thick, 57 mm internal dia. at the flange, with a hole 32 mm in the centre. Finally, a piece of clean glass 64 mm<sup>2</sup>  $\times$  9.5 mm thick was placed on top of the locating ring, the whole process of assembly being carried out without delay.



The cell was now left undisturbed throughout the period of the test.

The detector paper was examined through the glass plate at regular intervals to identify the moment of formation of blue spots. The mustard gas penetration time is taken as the interval in minutes between laying the test piece disc on the spacer ring and the first indication of the appearance of blue spots.

If it is proposed to carry out further tests during the day, the 50 mm glass disc should be replaced over the vapour source after first applying a further 3  $\mu$ L (app. 4 mg) of mustard gas to the white cotton drill. Then it is left for 30 minutes before a further test is carried out. At the end of the day, the white cotton drill must be destroyed and the cell components thoroughly decontaminated, the brass components by boiling in water and the glass component by soaking overnight in sodium hypochlorite solution (1 volume of commercial solution containing 10 per cent available chlorine diluted with required volumes of water).

(b) *Detector paper preparation*—The detector paper, which must be used on the same day of its preparation, was made in two stages. In the first stage, strips of Whatman No. 1 filter paper were dipped in a 0.05 per cent solution of Congo Red and allowed to dry in a fume free atmosphere. Detector paper at this stage could be stored up to six months. On the day of use the paper was prepared by spotting SD (spot disc) reagent on it. This was conveniently achieved by pricking pin-holes (approx. 4 per square centimeter) in a sheet of cellulose acetate, placing the perforated sheet over the Congo Red paper and gently rubbing the surface of the sheet with cotton pad soaked in SD reagent solution.

(c) *Synthesis of SD reagent*—SD reagent (2, 4-dichlorophenylbenzoylchloroimide) was synthesized using the standard method<sup>8</sup> by chlorinating the 2, 4-dichlorobenzanilide with bleaching powder in acetic acid-water system.

## 2. Closed chamber HDBTT (Sulphur mustard breakthrough time) test<sup>2</sup>

Test sample was conditioned with sulphur mustard at a temperature 20°C before testing. 3 mL of methyl red (indicator solution) was poured into a glass crucible with a wide rim. The circular sample, 5 cm dia., was placed over the top of the crucible and sealed with bees wax. The distance between the sample and the surface of the indicator solution was 5 mm. A ring (height: 10 mm, inside dia.: 20 mm) was placed in the centre of the sample and sealed with wax. 3  $\times$  1  $\mu$ L HD was applied on the surface inside the ring (1  $\mu$ L per cm<sup>2</sup>), covered the ring with a lid and sealed with wax.

HD penetration time was the time taken by HD to discolour the methyl red after penetrating the fabric material.

*Indicator solution*—100 mg of methyl red was dissolved in 100 ml alcohol. 10 ml of this solution was diluted to 1.0 L with distilled water. 6  $\pm$  0.1 mL of 0.01 N borate was added to obtain a pH between 6.4 to 6.6. The prepared solution lasts one week. The pH must be checked every time before use and adjusted, if need be, by adding borate buffer drop by drop.

## 3. Static Diffusion Method<sup>4</sup>

Over a glass plate the detector paper (Congo Red paper spotted with SD reagent) was placed above which the test sample, 5 cm dia. was kept and sealed with wax. 118  $\mu$ L HD was now placed over the filter paper (1 cm<sup>2</sup>, square in shape) lying over the test specimen in the centre. The test specimen was enclosed with glass petri dish and sealed with wax. This test assembly was placed in a chamber of constant temperature 37  $\pm$  0.5°C and was observed for blue colour formation in the detector paper. The interval between the instant the mustard was placed on the sample and the first appearance of blue colour on the spotted portion of the indicator paper was termed the mustard resistance of the material.

## 4. TNO GC Method<sup>3</sup>

This method was devised as a confidence building laboratory test as it provides quantitation of permeated sulphur mustard through the fabric. The method is as follows. Complete clothing assembly combined with a polyethylene film (0.015 mm) was positioned on a horizontally oriented glass cell. The specimen was fixed with a glass ring of 3-5 mm height and rubber bands. The exposed surface area of the sample was 1.5 cm<sup>2</sup>. There was a flow of air parallel to the surface of the specimen at 0.5 M/s. A droplet of 1  $\mu$ L mustard gas was placed onto the outer fabric corresponding with a contamination density of 8.3 g/m<sup>2</sup>. A flow of air (6 L/h) underneath the polyethylene film transported the penetrated mustard gas vapours to a bubbler. The vapour was trapped in an organic solvent (diethylsuccinate/diethylphthalate).

Solution of sulphur mustard thus obtained was analysed for HD quantitation by GLC technique using Chemito Chromatograph Model No. 3865. BP-5 wide bore capillary column (25 m  $\times$  0.53 mm) in conjunction with FID detector. Oven temperature, injection port temperature and detector temperature were 110°C, 175°C and 250°C respectively. Under these conditions HD eluted at 2.4 minutes.



### 5. Multiple SD test

The permeable protective clothing samples, which gave a very high HDBTT value were tested using permeation assembly by the following multiple SD test. Over a glass plate (5 cm × 5 cm) containing detector paper, fabric sample (3 cm × 3 cm) was placed and sealed with wax. 9 drops of HD 1 µL each per sq.cm of fabric were then placed and covered with a glass petri dish. Every 24 hr sulphur mustard drops were applied till it broke through the fabric. HDBTT was the time taken by detector paper for changing its colour.

### Results and Discussion

The methods so far mentioned were used for performance evaluation and quality control and the results for permeable and impermeable protective clothing (indigenous and imported) are described in Tables 1-5.

Table 1 describes the HDBTT results along with the quantities of HD collected in 6 hr both for the indigenous and imported fabrics including activated charcoal cloth. To develop indigenous permeable

protective suiting different carbons of varying characteristics were used in different proportions of adhesive polychloroprene and a few of the parameters are detailed in Table 2. Tables 1 and 2 indicate that the permeation assembly test not only provides a tool to measure protective potential but helps in monitoring the quality also as suitable and optimum carbon-adhesive ratio (70:30) was adjusted by this method only. However, TNO GC method offers quantitation of broken through HD through fabrics and enables one to be confident about the usage of clothing if they pass this test. Closed chamber HD test fails to make impact as shown by the values in Table 3 and that by varying HD quality significantly (20 times) does not result in appreciable lowering of HD BTT value. Because of this drawback the method was not used to evaluate the clothing for its chemical protection.

Adhesive bonded carbon when coated on non-woven fabric provides a low HD BTT value when compared to imported activated charcoal cloth which could be ascribed to the blockage of the pores of carbon by adhesive molecules. This results in a drastic reduction of surface area (1650 m<sup>2</sup>/g to 40

Table 1—HD BTT results of protective clothing

Sample	Source	Surface area (m <sup>2</sup> /g)	HD BTT <sup>a</sup> hr-min	HD <sup>b</sup> collected in 6 hr (µg/1.5)
Carbon coated non-woven fabric with nylon fabric as outer fabric	DMSRDE, Kanpur	40	10-37	Nil
-do-	-do-	40	10-5	Nil
-do-	-do-	40	10-6	Nil
-do-	-do-	40	10-53	Nil
-do-	-do-	40	10-51	Nil
-do-	-do-	40	10-45	Nil
-do-	-do-	—	0-59	59
-do-	Britain	—	1-40	25
Spherical carbon coated/laminated/FM4/250FL-Kevlar	Saratoga, USA	—	—	25
Activated charcoal cloth SC 3938C/FM4/250FL-Kevlar	Britain	774.8	324-15	Nil
-do-	-do-	787.7	115-45	Nil
ACC FM1/250	Britain	654.2	117-36	Nil
Activated charcoal cloth FM3/250L	-do-	563.35	266-21	Nil
-do-	-do-	—	252-48	Nil
CCL MK II Combat Uniform Material	-do-	—	252-48	Nil
-do-	-do-	—	252-48	Nil
FR Cotton/FM3/250FL/FR Cotton	-do-	521.36	132-19	Nil
-do-	-do-	521.36	132-19	Nil
ACC FM4/250FL Kevlar	-do-	38	4-40	Not done
Carbon coated non-woven fabric	-do-	38	4-40	Not done

a—Av. (Average) of ten samples and method used was permeation assembly test.

b—The employed method was TNO GC.



Table 2—Evaluation of carbon coated non-woven fabric obtained by processing parameter

Sample	Process parameter	HD BTT hr-min	Surface area of carbon used (m <sup>2</sup> /g)
Carbon coated non-woven fabric	200 mesh size carbon slurry coated on fabric by spreading	0-43.6	1650
-do-	200 mesh size carbon slurry coated on fabric by spraying	2-53	"
-do-	Ball milled the 200 mesh size carbon slurry for 48 hr coated on fabric by spreading	0-34.8	"
-do-	Ball milled the 200 mesh size carbon slurry for 48 hr and coated fabric by spraying	0-33.6 (av. of 9) 1-5 (av. of 3)	"
-do-	Ball milled the 200 mesh size carbon slurry for 96 hr and coated on fabric by spreading	0-27.6	"
-do-	Ball milled the 200 mesh size carbon slurry for 96 hr and coated of fabric by spraying	1-13.6	"
-do-	Slurry of carbon and adhesive in ratio 70 to 30 and applied two coats on fabric	2-58	"
-do-	-do- with pressure of 5 tonnes/inch <sup>2</sup> for 10 min	2-0	"
Carbon coated non-woven fabric	Applied 2 coats of slurry with pressure, 20 tonnes/inch <sup>2</sup> for 10 min	1-50	"
-do-	Slurry of carbon and adhesive in the ratio (60 to 40) and applied 2 coats on fabric	2-16	"
-do-	Carbon and adhesive ratio in slurry was kept 65 to 35 and applied 2 coats on fabric	1-13	"

Table 3—Evaluation of permeable protective clothing against HD using closed chamber HD drop test method at 20°C

Sample	HD conc	HD BTT hr-min
Charcoal coated non-woven fabric with flame proof and oil repellent nylon fabric as outer layer from DMSRDE, Kanpur	3 × 1 µL drops	0-39
-do-	3 × 1 µL drops	0-39
-do-	3 × 20 µL drops	0-22
-do-	3 × 20 µL drops	0-21

m<sup>2</sup>/g) in carbon coated non-woven fabric. However charcoal cloth (low in strength) after lamination on kevlar provides the required strength to the carbon fibres and gives a very high HD BTT value (Table 1). Due to its high chemical protection value reported in Table 1 this fabric was subjected to multiple SD test in our establishment and results are shown in Table 4. The results indicate that sulphur mustard breakthrough occurred after the third application of the agent in all the samples studied. It can be inferred from these results that the activated charcoal cloth can be used a

Table 4—Evaluation of activated charcoal cloth, British, against HD using multiple SD test, at temp. 20 ± 1°C

Sample	HD BTT hr-min	Remarks
SC 3938C/FM4/250/FL/Kevlar	120-16	HD penetration occurred, 16 min after sixth application of HD
ACCFM 1/250	63-23	HD penetration occurred, 15 hr and 23 min after third application of HD reagent
FM-3/250/FL	64-20	HD penetration occurred, 16 hr 20 min after third application of HD
CCL MK III combat uniform materials	72-58	HD penetration occurred, 58 min after fourth application of HD
FR Cotton/FM 3/250 FL/FR cloth	50-25	HD penetration occurred 2 hr and 25 min after third application of HD
ACCFM4/250 FL/Kevlar	96-30	HD penetration occurred 30 min after fifth application of HD

number of times and for a longer period. It will be worth mentioning that its utility is still to be ascertained mainly due to the fragile characteristic of activated charcoal cloth.



Table 5—Performance evaluation of impermeable protective material

Sample	Thickness (mm)	Source	HD BTT <sup>a</sup> hr-min
One side neoprene and other side butyl rubber coated nylon fabric	0.31	DMSRDE, Kanpur	1-19
-do-	0.30	-do-	1-15
-do-	0.36	-do-	2-34
-do-	0.33	-do-	2-03
-do-	0.34	-do-	2-09
-do-	—	Korea	0-55

a—Static diffusion test was employed to evaluate the impermeable protective clothing.

Table 5 indicates that the static diffusion test is highly useful in evaluating and controlling the quality of impermeable protective clothing. This can be seen from the data that by varying the thickness of rubber coating on nylon fabric HD BTT values change significantly. Results indicate that the thicker the fabric, more will be the discomfort and heat stress. Approximately 0.30 mm was found to be the optimum thickness of the fabric to provide the stipulated one hour chemical protection.

### Conclusion

Permeation assembly and static diffusion test

methods enabled us develop the permeable and impermeable protective clothing comparable to their foreign counterparts. The study also indicated that TNO GC method could be most suitably used as a confidence building technique.

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## Concentrational changes in tomato juice of new hybrids

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Concentrational changes in tomato juice of six new high yielder cultivars registered a tangible increase in reducing sugars with marginal change in pH, acidity, pectin and tannin. Ascorbic acid was the maximum sufferer with more pronounced losses (50.7%) in open vat than under vacuum (46.8%) evaporation. Lycopene remained almost constant, retaining native intense red colour of new hybrids in the resulting concentrates.

Fresh tomato and its product are important culinary items of daily use. New high yielding disease resistant hybrids and non-hybrids are being continuously developed by the vegetable breeders throughout the world. Such new varieties require extensive testing prior to processing. Present investigation deals with the physico-chemical changes occurring during the manufacture of juice concentrate from new promising high yielder tomato hybrids grown under Punjab conditions.

### Materials and Methods

Five high yielder new Indo-American/American hybrids and one new non-hybrid along with control (*Punjab chhuhara*) were picked at the red ripe stage during peak harvesting period (May-June) of the Punjab grown main season tomato crop. Their juice was extracted,<sup>1</sup> hot (85°C), packed in 650 ml bottles, processed (45 min) in boiling water tanks followed by their immediate cooling. Processed juice was held at room temperature till concentration in a steam jacketed kettle as well as under vacuum at 27-30" Hg (0.95-1 kg/cm<sup>2</sup>) at 50°-55°C. Samples were drawn at varied degree of concentration and analyzed<sup>1</sup>.

### Results and Discussion

**Solids**—Total soluble solids (TSS) increased with concentration (Tables 1-7). Maximum strength of the concentrated mass was 20°Brix under vacuum, beyond which the product lost its fluidity and posed serious problems regarding its rheology, therefore, further concentration of juice was abandoned. Open pan concentrate also showed notable charring beyond 21°Brix. Therefore, juices could be concentrated only up to 20°Brix by both the processes so as to maintain their viscosity and to retain characteristic bright red colour in the finished

product. There was parallel improvement in total solids as the concentration advanced. Mean total solids improved from 6.01 to 21.95 and 22.45 per cent for open and vacuum concentrates. Increase in total solids showed uniform trend in all the new cultivars undergoing evaporation irrespective of the method employed.

Reducing sugars increased during thermal processing. Per cent increase depended upon the variety and processing treatment given. Open vat cooking recorded higher inversion than their counterparts. The mean improvement in reducing sugars was 14.3 per cent in open vat and 12.2 per cent under vacuum on moisture free basis. Total sugars declined marginally from mean initial level (61.61%) to 61.20 per cent. Degraded sugars are known to participate in browning reactions<sup>2</sup>.

**Acidity and pH**—Per cent loss of acidity was 4.06 under vacuum and 4.82 for open pan concentrate resulting slight change in pH with respective increase to 4.43 and 4.36 from the initial pH level of 4.36 (Table 1-7). Funseca and Luh<sup>3</sup> noticed decline in titrable acidity<sup>4</sup> with simultaneous enhancement in pH upon increased heat treatment during concentration of tomato juice. Reactions causing loss of fruit acids during concentration have already been demonstrated<sup>5</sup>.

**Ascorbic acid (AA)**—Tremendous decline in AA occurred as the concentration advanced. Extensive loss of AA in the open vat (50.7%) was higher than under vacuum (46.8%) (Tables 1-7). Decline was more pronounced during later stages of evaporation. Occurrence of more losses at elevated temperature has already been proved<sup>3</sup>. However, Setty *et al.*<sup>6</sup> noticed comparatively less loss of AA ranging from 0.9 per cent for *Hehos* to 18 per cent for *Drubuza* on initial content basis while preparing paste from



Table 1—Effect of concentration on physico-chemical characteristics of *Punjab chhuhara* tomato juice

Composition	Initial	10	TSS°Brix				
			15 Open Concentrated	20	15	15 Vacuum Concentrated	20
TS %	5.87	12.50	18.60	21.15	12.60	18.92	21.26
pH	4.40	4.40	4.42	4.43	4.41	4.43	4.44
Acidity %	0.51	1.07	1.58	1.77	1.08	1.61	1.80
	(6.68)	(8.56)	(8.50)	(8.36)	(8.57)	(8.51)	(8.46)
Reducing sugars %	2.04	4.45	6.72	7.87	4.41	6.69	7.65
	(34.75)	(35.60)	(36.12)	(37.21)	(35.00)	(35.35)	(35.98)
Non-reducing sugars %	1.57	3.26	4.79	5.29	3.37	5.03	5.63
	(26.74)	(26.08)	(25.75)	(25.01)	(26.74)	(26.58)	(26.48)
Total sugars %	3.70	7.89	11.77	13.44	7.96	11.99	13.58
	(63.03)	(63.12)	(63.27)	(63.27)	(63.54)	(63.37)	(63.87)
Ascorbic acid mg/100 g	19.26	25.58	29.75	32.04	26.31	34.20	35.26
	(334.2)	(319.8)	(238.0)	(151.5)	(208.8)	(186.8)	(165.9)
Pectin as CaPec %	0.15	0.32	0.46	0.52	0.32	0.47	0.52
	(2.55)	(2.48)	(2.47)	(2.45)	(2.53)	(2.48)	(2.48)
Tannin (mg/ml)	0.33	0.35	0.39	0.51	0.57	0.41	0.53
Lycopene mg/100 g	3.56	7.57	11.25	12.77	7.64	11.45	12.85
	(60.64)	(60.56)	(60.48)	(60.37)	(60.63)	(60.51)	(60.44)
Tintometric colour units:							
Red	20.0	22.5	28.0	27.0	24.4	28.8	28.1
Yellow	15.0	13.0	20.0	20.0	16.0	24.0	20.0
Blue	0.2	1.0	1.8	2.2	0.9	1.2	1.7

Figures in parentheses are on dry matter basis

Table 2—Effect of concentration on physico-chemical characteristics of *NH-15* Hybrid tomato juice

Composition	TSS°Brix						
	Initial	10	Open		Vacuum		
			15	20	15	15	20
			Concentrated	Concentrated			
TS %	6.82	10.40	15.08	21.66	11.94	17.01	22.77
pH	4.38	4.40	4.40	4.41	4.40	4.41	4.42
Acidity %	0.69	1.04	1.49	2.10	1.20	1.61	2.23
	(10.11)	(10.00)	(9.88)	(9.70)	(10.05)	(9.91)	(9.79)
Reducing sugars %	2.15	3.47	5.22	7.82	3.83	5.78	8.00
	(31.52)	(33.38)	(34.61)	(36.10)	(32.07)	(33.98)	(35.15)
Non-reducing sugars %	1.82	2.61	3.63	4.95	3.15	4.20	5.44
	(26.68)	(25.09)	(24.07)	(22.85)	(24.38)	(24.69)	(23.89)
Total sugars %	4.07	6.22	9.05	13.04	7.15	10.21	13.73
	(59.87)	(59.80)	(60.01)	(60.20)	(59.88)	(60.02)	(60.29)
Ascorbic acid mg/100 g	22.21	27.52	32.52	37.52	30.07	34.88	43.89
	(325.6)	(264.6)	(215.6)	(173.2)	(251.8)	(205.5)	(192.7)
Pectin as CaPec %	0.16	0.24	0.35	0.49	0.28	0.39	0.52
	(2.34)	(2.30)	(2.32)	(2.26)	(2.34)	(2.29)	(2.28)
Tannin (mg/ml)	0.44	0.46	0.52	0.61	0.48	0.55	0.67
Lycopene mg/100 g	4.32	6.58	9.53	13.67	7.56	10.76	14.38
	(63.34)	(63.26)	(63.19)	(163.11)	(63.31)	(63.25)	(63.15)
Tintometric colour units:							
Red	27.0	32.5	32.0	31.0	30.1	33.0	32.8
Yellow	17.0	16.0	20.0	23.0	14.0	20.0	20.7
Blue	0.2	0.9	1.2	1.9	0.6	1.0	1.5

Figures in parentheses are on dry matter basis



Table 3—Effect of concentration on physico-chemical characteristics of *NH-25* Hybrid tomato juice

Composition	Initial	TSS°Brix					
		10	15	20	15	15	20
			Open Concentrated		Vacuum Concentrated		
TS %	6.87	10.55	15.50	21.80	11.61	16.24	22.33
pH	4.43	4.43	4.44	4.45	4.39	4.40	4.42
Acidity %	0.55	0.83	1.20	1.66	0.92	1.28	1.74
	(8.00)	(7.86)	(7.74)	(7.61)	(7.92)	(7.88)	(7.79)
Reducing sugars %	2.19	3.40	5.43	7.86	3.72	5.61	7.96
	(31.87)	(32.22)	(35.03)	(36.05)	(32.04)	(34.54)	(35.64)
Non-reducing sugars %	1.81	2.77	3.68	5.03	3.07	3.95	5.26
	(26.34)	(26.25)	(23.74)	(23.07)	(26.44)	(24.32)	(23.55)
Total sugars %	4.10	6.32	9.31	13.16	6.96	9.77	13.50
	(59.67)	(59.90)	(60.06)	(60.36)	(59.94)	(60.16)	(60.45)
Ascorbic acid mg/100 g	22.17	24.52	31.99	36.99	26.08	29.50	36.40
	(322.7)	(232.4)	(206.3)	(169.6)	(224.6)	(181.6)	(163.0)
Pectin as CaPec %	0.17	0.26	0.37	0.52	0.28	0.39	0.54
	(2.47)	(2.46)	(2.38)	(2.38)	(2.41)	(2.40)	(2.41)
Tannin (mg/ml)	0.42	0.45	0.53	0.59	0.47	0.55	0.63
Lycopene mg/100 g	5.74	8.80	12.91	18.15	9.69	13.53	18.60
	(83.55)	(83.41)	(83.24)	(83.25)	(83.46)	(83.31)	(83.30)
Tintometric colour units:							
Red	28.0	30.0	30.0	32.0	32.1	34.0	33.0
Yellow	17.0	10.0	20.0	23.0	17.0	20.0	20.6
Blue	0.5	1.1	1.7	2.9	0.9	1.3	1.9

Figures in parentheses are on dry matter basis

Table 4—Effect of concentration on physico-chemical characteristics of *NH-2476* Hybrid tomato juice

Composition	Initial	TSS°Brix					
		10	15	20	10	15	20
			Open Concentrated		Vacuum Concentrated		
TS %	5.80	10.42	16.72	20.63	11.04	17.10	21.51
pH	4.37	4.37	4.38	4.40	4.36	4.37	4.39
Acidity %	0.66	1.16	1.83	2.20	1.25	1.86	2.32
	(11.37)	(11.13)	(10.94)	(10.66)	(11.32)	(10.87)	(10.78)
Reducing sugars %	1.90	3.45	5.93	7.64	3.65	6.09	7.79
	(32.75)	(33.10)	(35.46)	(37.03)	(33.06)	(35.08)	(36.21)
Non-reducing sugars %	1.69	2.98	4.37	5.08	3.17	4.47	5.49
	(29.13)	(28.59)	(26.13)	(24.62)	(28.71)	(26.14)	(25.52)
Total sugars %	3.68	6.59	10.54	12.99	6.99	10.80	13.57
	(63.44)	(63.24)	(63.08)	(62.96)	(63.31)	(63.15)	(63.08)
Ascorbic acid mg/100 g	16.21	22.14	29.90	35.64	23.39	31.24	37.96
	(279.4)	(212.4)	(178.2)	(172.7)	(211.8)	(182.6)	(176.4)
Pectin as CaPec %	0.21	0.37	0.59	0.72	0.40	0.61	0.76
	(3.62)	(3.55)	(3.52)	(3.49)	(3.62)	(3.56)	(3.53)
Tannin (mg/ml)	0.36	0.39	0.49	0.54	0.42	0.50	0.56
Lycopene mg/100 g	3.51	6.30	10.06	12.41	6.68	10.30	12.95
	(60.51)	(60.46)	(60.16)	(60.15)	(60.58)	(60.29)	(60.20)
Tintometric colour units:							
Red	26.0	33.0	32.0	31.0	34.0	34.0	32.0
Yellow	18.0	10.0	13.0	20.0	11.0	20.0	30.6
Blue	0.2	0.8	1.2	1.9	0.6	1.0	1.6

Figures in parentheses are on dry matter basis



Table 5—Effect of concentration on physico-chemical characteristics of *NH-3025* Hybrid tomato juice

Composition	Initial	TSS°Brix					
		10	15	20	10	15	20
		Open Concentrated			Vacuum Concentrated		
TS %	5.98	9.86	15.42	22.63	11.96	16.11	22.00
pH	4.37	4.38	4.40	4.42	4.38	4.39	4.40
Acidity %	0.52	0.83	1.29	1.87	1.01	1.35	1.90
	(8.69)	(8.41)	(8.36)	(8.26)	(8.44)	(8.37)	(8.30)
Reducing sugars %	1.55	2.61	4.27	6.64	3.14	4.62	6.64
	(25.91)	(26.47)	(27.64)	(29.34)	(21.25)	(28.67)	(28.99)
Non-reducing sugars %	2.00	3.24	4.89	6.80	3.97	4.97	6.99
	(33.44)	(32.86)	(31.71)	(30.04)	(33.19)	(30.85)	(30.52)
Total sugars %	3.66	6.03	9.42	13.80	7.32	9.86	14.00
	(61.20)	(61.18)	(61.15)	(60.98)	(61.20)	(61.20)	(61.16)
Ascorbic acid mg/100 g	21.75	26.58	32.32	36.37	30.75	34.34	42.86
	(363.7)	(269.5)	(209.5)	(160.7)	(257.1)	(213.1)	(187.1)
Pectin as CaPec %	0.13	0.21	0.33	0.47	0.26	0.34	0.48
	(2.17)	(2.12)	(2.14)	(2.04)	(2.17)	(2.11)	(2.09)
Tannin (mg/ml)	0.40	0.44	0.52	0.59	0.45	0.52	0.61
Lycopene mg/100 g	3.58	9.19	14.36	21.05	11.15	15.01	21.32
	(93.31)	(93.12)	(93.01)	(93.22)	(93.17)	(93.17)	(93.10)
Tintometric colour units:							
Red	28.0	33.0	30.0	30.7	34.0	30.0	33.0
Yellow	15.0	14.0	20.0	11.0	11.0	21.0	23.0
Blue	0.0	0.7	1.1	1.9	0.4	0.9	1.3

Figures in parentheses are on dry matter basis

Table 6—Effect of concentration on physico-chemical characteristics of *NH-3027* Hybrid tomato juice

Composition	Initial	TSS°Brix					
		10	15	20	10	15	20
		Open Concentrated			Vacuum Concentrated		
TS %	5.29	10.40	16.30	22.93	11.46	16.72	23.21
pH	4.36	4.38	4.38	4.39	4.38	4.40	4.41
Acidity %	0.54	1.04	1.62	2.26	1.15	1.75	2.29
	(10.22)	(10.00)	(9.93)	(9.86)	(10.03)	(9.93)	(9.86)
Reducing sugars %	1.67	3.39	5.63	8.17	3.70	6.01	8.16
	(31.62)	(32.61)	(34.56)	(35.63)	(32.28)	(34.10)	(35.15)
Non-reducing sugars %	2.00	3.84	5.70	7.75	4.27	6.26	8.02
	(37.87)	(36.92)	(34.96)	(33.79)	(37.26)	(35.52)	(34.55)
Total sugars %	3.78	7.44	11.64	16.33	8.20	12.60	16.59
	(71.59)	(71.53)	(71.41)	(71.21)	(71.55)	(71.50)	(71.49)
Ascorbic acid mg/100 g	22.19	28.89	35.89	41.67	30.35	38.29	45.74
	(420.2)	(277.7)	(219.8)	(181.7)	(264.8)	(217.3)	(199.6)
Pectin as CaPec %	0.17	0.33	0.51	0.71	0.36	0.55	0.72
	(3.21)	(3.17)	(3.12)	(3.09)	(3.14)	(3.12)	(3.10)
Tannin (mg/ml)	0.39	0.45	0.55	0.60	0.47	0.56	0.59
Lycopene mg/100 g	4.88	9.60	15.02	21.11	10.58	16.25	21.38
	(92.42)	(92.30)	(92.14)	(92.06)	(92.32)	(92.22)	(92.10)
Tintometric colour units:							
Red	28.0	34.0	30.0	32.0	30.0	34.0	33.0
Yellow	16.0	26.0	28.0	30.0	10.0	13.0	23.0
Blue	0.0	0.5	1.0	1.7	0.3	0.7	1.2

Figures in parentheses are on dry matter basis



Table 7—Effect of concentration on physico-chemical characteristics of 1-7-1-1 tomato juice

Composition	TSS°Brix						
	Initial	10	15	20	10	15	20
			Open	Concentrated		Vacuum	Concentrated
TS %	5.51	10.64	16.80	22.03	11.24	17.29	22.29
pH	4.43	4.44	4.45	4.45	4.43	4.44	4.46
Acidity %	0.37	0.70	1.07	1.38	0.74	1.10	1.40
	(6.71)	(6.57)	(6.36)	(6.26)	(6.58)	(6.36)	(6.28)
Reducing sugars %	1.71	3.44	5.86	7.95	3.67	5.88	8.04
	(31.03)	(32.33)	(34.88)	(36.08)	(32.65)	(35.00)	(36.06)
Non-reducing sugars %	1.81	3.34	4.86	6.08	3.50	5.14	6.16
	(32.84)	(31.39)	(28.92)	(27.59)	(31.13)	(29.72)	(27.63)
Total sugars %	3.62	6.96	10.98	14.35	7.36	11.30	14.53
	(65.69)	(65.41)	(65.35)	(65.13)	(65.48)	(65.35)	(65.18)
Ascorbic acid mg/100 g	19.21	25.26	30.83	35.56	26.61	35.45	44.21
	(348.6)	(237.4)	(183.5)	(175.0)	(236.7)	(205.0)	(198.3)
Pectin as CaPec %	0.19	0.36	0.56	0.73	0.39	0.59	0.75
	(3.44)	(3.38)	(3.33)	(3.31)	(3.46)	(3.41)	(3.36)
Tannin (mg/ml)	0.37	0.41	0.50	0.57	0.43	0.51	0.57
Lycopene mg/100 g	4.40	8.48	13.38	17.51	8.96	13.78	17.73
	(79.85)	(76.69)	(79.64)	(79.48)	(79.71)	(79.69)	(79.54)
Tintometric colour units:							
Red	30.0	35.0	28.0	34.0	30.0	31.0	35.0
Yellow	16.0	20.0	22.0	30.0	20.0	23.0	28.6
Blue	0.0	0.7	1.1	1.6	0.4	0.8	1.2

Figures in parentheses are on dry matter basis

Bulgarian tomatoes. Degraded AA is known to enter discolouration mechanism via furfural<sup>2</sup> formation.

**Pectin and tannin**—Though some losses occurred in the pectin fraction (Tables 1 to 7), yet the concentrated mass retained sufficient pectin to maintain the rheological quality of the product. Pectin declined slightly during processing. Losses in pectin were more pronounced for open vat (3.54%) preparations than vacuumized (2.48%) products. Notable (Tables 1-7) losses in pectin occurred when concentration exceeded 15°Brix.

Varietal sequence of pectin retention was: *NH-2476* > *1-7-1-1* > *NH-3027* > *Punjab chuhara* > *NH-25* > *NH-3025* (dwb). Concentrated product contained 2.73 per cent pectin on dry weight basis or 0.60 per cent on as is basis. Occurrence of concentrational losses in pectin at elevated temperature has already been reported<sup>3</sup>. Paste (26.5% TS) prepared from ripe tomatoes was found to contain more water soluble pectin but less total pectin<sup>7</sup>.

Tannin content ranged from 0.33 to 0.44 mg/ml of juice which increased due to concentration, however, the increase was unparallel to the degree of concentration. Comparatively more tannin was retained under vacuum as compared to their counterparts, irrespective of the variety undergoing thermal processing.

**Lycopene and tintometric colour**—Lycopene pigment ranged from 12.41 to 21.11 mg/100 g in the open pan concentrate while it rose to 12.95 to 21.38

mg/100 g under vacuum (Tables 1-7). *NH-3027* vacuum concentrated juice recorded maximum lycopene followed by *NH-3025*, *NH-25*, *1-7-1-1*, *NH-15*, *Punjab chuhara* and *NH-2476*. Similar trend emerged out for open pan cooking. The hybrids under investigation were selected carefully out of large number of collections and were having bright red colour characteristic of the fruit at the time of harvest, apart from their high yield potentials. The native intense colour was retained in the juices and resulting concentrates and was also reflected by the quantity of lycopene as well as high tintometric red colour readings of the finished product. The study highlighted that all the varieties excepting *NH-2476* under product testing were superior in their red pigment (lycopene) than the control and were found suitable for the manufacture of concentrate/paste as far as retention of tomato pigment is concerned. Setty *et al.*<sup>6</sup> also recorded similar impressions regarding status of red pigment while preparing 28°Brix paste from new varieties of Bulgarian origin.

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## Inhibiting corrosion of carbon-steel metal in distillation process

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The distillation unit separates the crude oil into various boiling range fractions. These fractions are further refined into finished products. The paper deals with the corrosion of C-steel metal during distillation of Gysume crude oil (vapour phase) at 100°, 150°, 200°, 250° and 300°C in absence and presence of 5% H<sub>2</sub>O. The effect of adding different inhibitors with various concentration on the corrosion of C-steel metal are studied.

Refining is the process which converts crude oil into the wide range of products required by the market<sup>1,2</sup>. Distillation is the main separation process it is a mass transfer unit operation used extensively in the petroleum and chemical industries for the separation of vapour and liquid mixtures on the bases of their volatility<sup>3,4</sup>.

Distillation units require considerable equipments in addition to the column proper, a condenser for the overhead vapours, a reflux drum to receive condensate, a reboiler to partially vapourize the bottom liquid, pumps to charge feed, reflux to withdraw products and automatic control equipment.

The most important problem in petroleum refining processes is the corrosion which deteriorate the equipment. Decomposition of impurities in crude oil during distillation into corrosive products<sup>5</sup> (e.g. H<sub>2</sub>S and HCl) must be known during refining processes.

### Experimental procedure

*Measurement of corrosion during distillation process*—The metal specimens (carbon steel previously described) were employed. The specimens were polished, degreased, weighed and were positioned at each of the three positions in the fractionating column. The main temperatures at each position were proceeding from the top 100°, 150° and 200°C. The metal specimens were removed successively after intervals (12 hr). All the experiments were carried out for 72 hr. Another specimens were immersed in crude oil flask. The distillation process takes place under atmospheric pressure.

The same process was repeated under reduced pressure of 10 mm Hg. The metal specimens were positioned at two positions.

The main temperature at each position were proceeding from the top 250° and 300°C. The metal specimens were removed successively after intervals (12 hr). The corrosion rate of metal specimens were determined using loss in weight method.

This process was repeated to study:

The effect of presence of water in crude oil on corrosion rate of the metal (carbon steel).

Effect of different types of inhibitors.

Neutralizer (Ammonia), at concentrations (4 to 10 ppm) on corrosion of carbon steel.

Ammonia (7 ppm) and chlorinated hexadecylamine inhibitor.

Heterocyclic compounds.

Naphthyl, 1,2,4 triazole-3-thione.

Benzyl, 1,2,4 triazole-3-thione, on corrosion of carbon steel (0.15% C).

The inhibitor efficiencies ( $I_E$ ) of C-steel metal were determined from comparison with the uninhibited corrosion rate using the formula.

$$I_E = r_0 - r_1 / r_0 \times 100$$

where,

$r_0$  is the corrosion rate of carbon steel without inhibitors and  $r_1$  is the corrosion rate in the presence of inhibitors.

### Results and Discussion

Gysume crude oil was distilled at atmospheric pressure. The results in Figs. 1-3 show that the initial rates of corrosion are somewhat lower than those found after longer periods of time. This may be due to the smooth surfaces of original metal specimens which may have decreased the rate of attack in the early stages.

The corrosion rates are usually low in the area



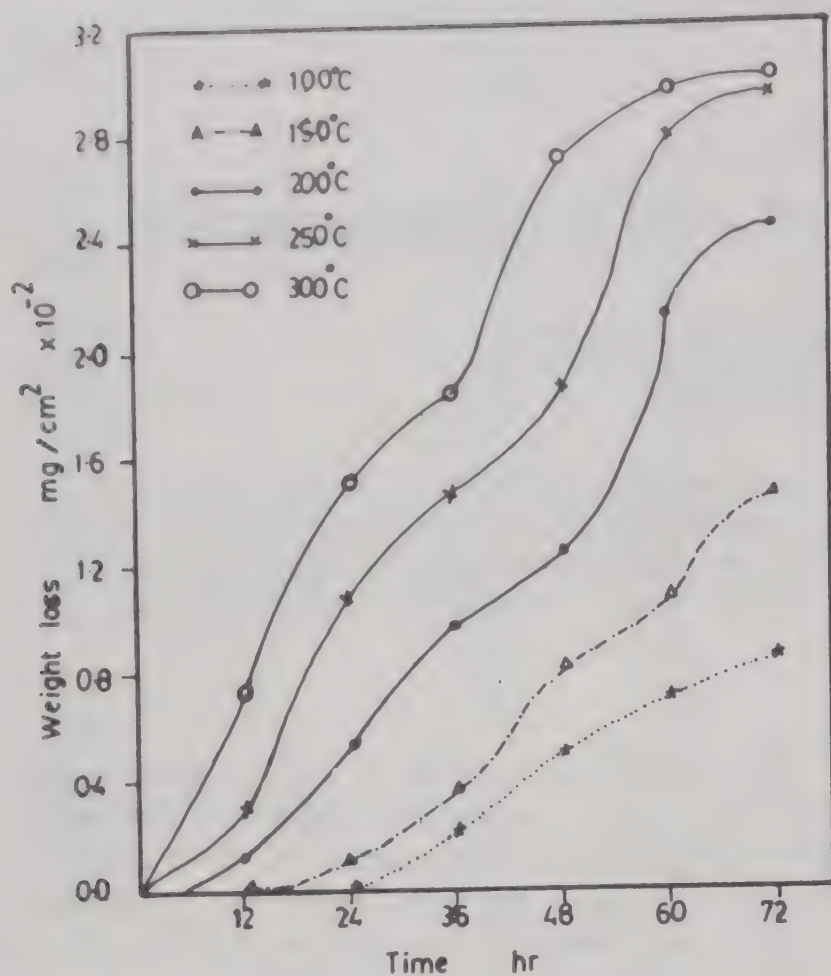


Fig. 1—Corrosion of C-steel during distillation of Gysume crude oil (V phase)

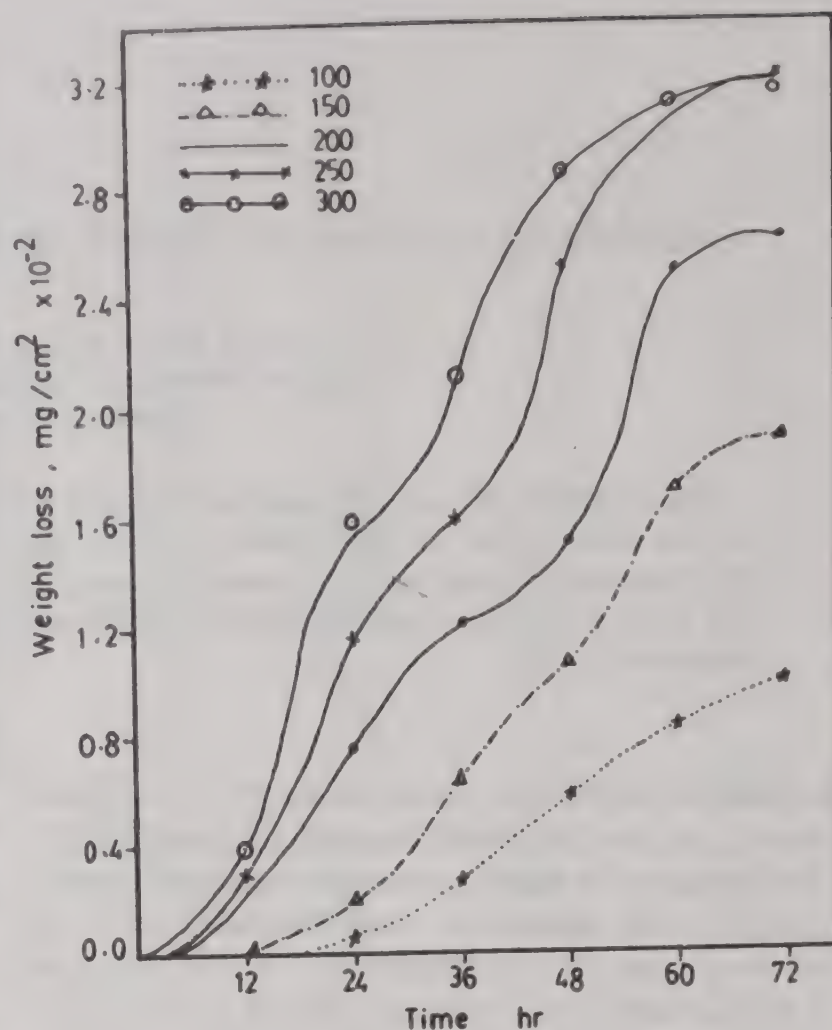


Fig. 2—Corrosion of C-steel during distillation of Gysume crude oil containing 5% H<sub>2</sub>O (V. phase)

below the flash zone. This may be due to the absence of any appreciable quantity of free hydrogen sulphide.

The data in Figs. 1-3 indicate that the corrosivities of carbon steel in the vapour phase are higher than those in the liquid phase. These deviations may be the result of splashing effects. The combined effects of volatile acids and volatile sulphur compounds (H<sub>2</sub>S) produced by decomposition of sulphur compounds tend to appear in the vapour phase and increasing its corrosivities rapidly.

Hydrogen sulphide is not the only corrodant present; hydrogen chloride which is formed by hydrolysis of unstable inorganic chloride in crude oil at high temperature is active and so it causes very rapid corrosion in heat exchangers and vapour lines<sup>6</sup>.

The high corrosion rates noted in the top part of the fractionating column at lower temperature are due to the temperature being below the dew point of water, thereby permitting the existence of aqueous hydrochloric acid resulting in rapid attack with metals.

The results in Figs. 1-3 indicate that the vapour corrosivity of the carbon steel metal drops and then shows a normal rise again. This is probably due to the presence of other gases (CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, hydrocarbons and water vapour) in the crude oil affecting the action of the hydrogen sulphide on the metal specimens

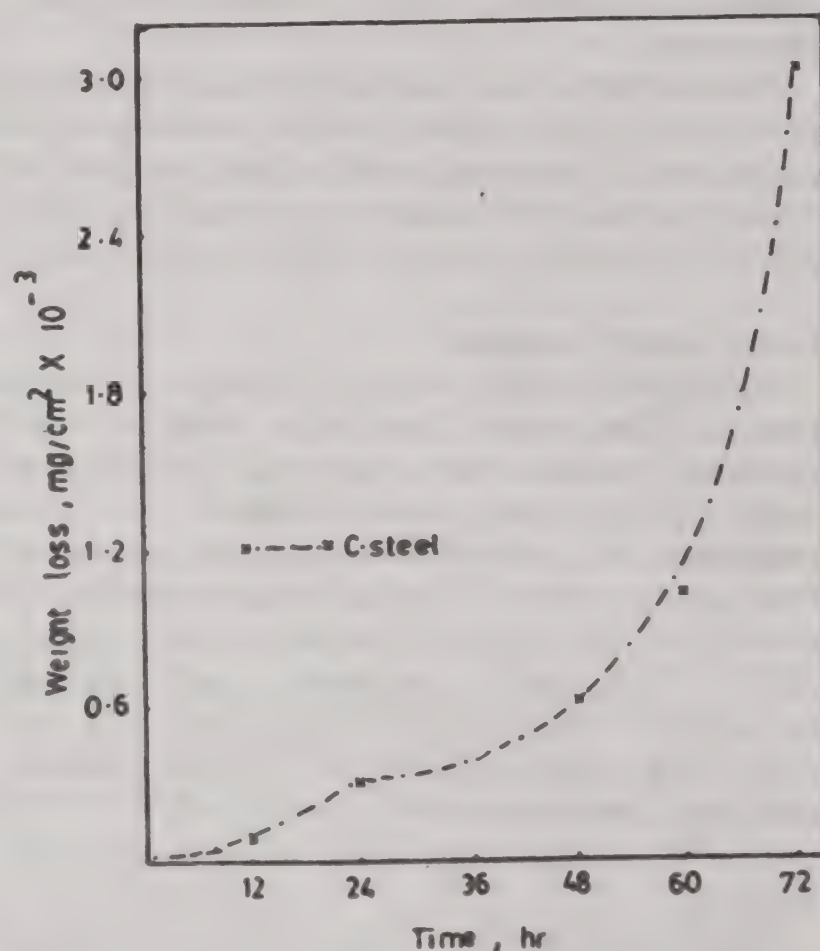


Fig. 3—Corrosion of C-steel metal in the liquid phase during distillation of Gysume crude oil



either by forming a dense protective film of material not acted on by hydrogen sulphide or by shifting the equilibria involved in the reaction to an unfavourable value. Variation in temperature during the distillation process would lead to a more or less complete destruction of the protective film by causing the formation of nonuniform cracked films which would permit attack if the underlying metal by hydrogen sulphide.

Fig. 3 indicates that in the liquid phase there is a sharp increase in corrosivity due to the formation of new non-volatile acid compounds by cracking. The corrosivity increased as it aged in the distilling flask.

The results in Figs. 1-3 illustrate that the amount of corrosion for the C-steel metal tends to approach a constant value for each temperature. To explain this phenomena Digby *et al.*<sup>7</sup> indicated that, when iron chloride and iron sulphide are form simultaneously in the surface, no continuous film of iron sulphide exists, and diffusion of iron ions from the metal surface to the gas-film interface through an iron sulphide layer can no longer take place because of the interposition of the poorly conducting iron chloride. It appeared that metal chloride in the film actually inhibits the reaction of hydrogen sulphide or active sulphur compounds with metal.

**Effect of addition of water on corrosion of C-steel metal**—The influence of addition of 5% H<sub>2</sub>O to the crude oil before distillation process was studied. It is found that the rate of corrosion is low at the initial stage of the distillation process, and increases with aging in the C-steel metal as shown in Fig. 2. The interpretation of this behaviour is that the moist hydrogen sulphide gave lower corrosion rate with metals than that of dry hydrogen sulphide. This is probably due to the formation of an oxide film by reaction of iron with water to give iron oxide which is more protective than the sulphide coating<sup>8</sup>. Since the various iron oxides are poor electronic conductors they do not appear to be effective catalysts for the sulphidation of iron in wet sulphur<sup>7</sup>.

The effect of water at higher stages in presence of hydrogen chloride, hydrogen sulphide and possibly some volatile acids produces a strongly acidic solution which is highly corrosive particularly to carbon steel. This is due to the fact that the carbon steel is relatively more easily oxidized by H<sup>+</sup> of dilute acids with the formation of hydrogen and ferrous salts.

**Inhibition of Corrosion**—Most of inhibitors used in distillation process are nitrogen compounds. To minimize the corrosivity of the overhead condensate during distillation process, neutralizers are added to control pH. Ammonia has been preferred because of

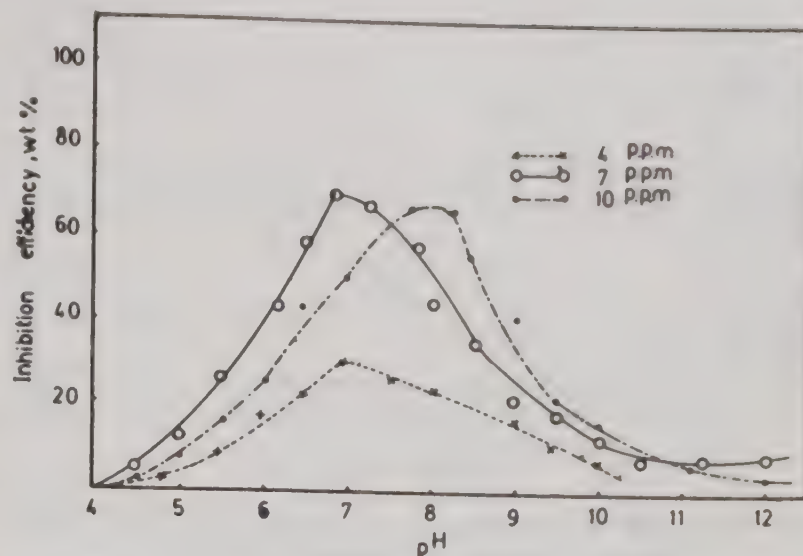


Fig. 4—Effect of ammonia on corrosion of C-steel

its ease of application, low cost, high solubility of its salts in water and can be removed readily. It is observed in Fig. 4 that the inhibitive efficiency of C-steel metal increased with addition of ammonia till it reach maximum value of about 70% at 7 ppm.

The amount of ammonia for protection varies inversely with pH. This usually holds true only up to a pH of about 7.5. Above this level most available products lose their effectiveness, not because of any excessive addition of ammonia as a neutralizer, but because of the generation of ammonia by the denitrification of the organic component of the charge stock. This means that the effectiveness of ammonia depends on the pH value.

The corrosion rate dropped to a very low value at pH 6.8 as shown in Fig. 4. If this limit is transgressed, the hydrogen evolution reaction will take place overleading to high corrosion rates and the destruction of inhibitor films.

At high temperature, the effectiveness of ammonia decreases as the quantity of HCl which is formed during the hydrolysis reaction increases. It was found that insufficient water could result in more sever corrosion of metal by concentrated NH<sub>4</sub>Cl solution<sup>9</sup>.

Fig. 5 illustrates the influence of addition of chlorinated hexadecylamine on the corrosion of C-steel in presence of ammonia during the distillation process. It can be seen that the rate of inhibition increases as compared with that obtained by addition of ammonia alone. The strong corrosion inhibition is probably due to the adsorption of the chlorinated hexadecylamine on the metal surface. The adsorbed film when augmented by sorbed hydrocarbons from the product stream forms a hydrophobic barrier which prevents attack by the aqueous corrodants normally contacting the metal surface<sup>9</sup>.

The results in Fig. 5 indicate that the inhibitive



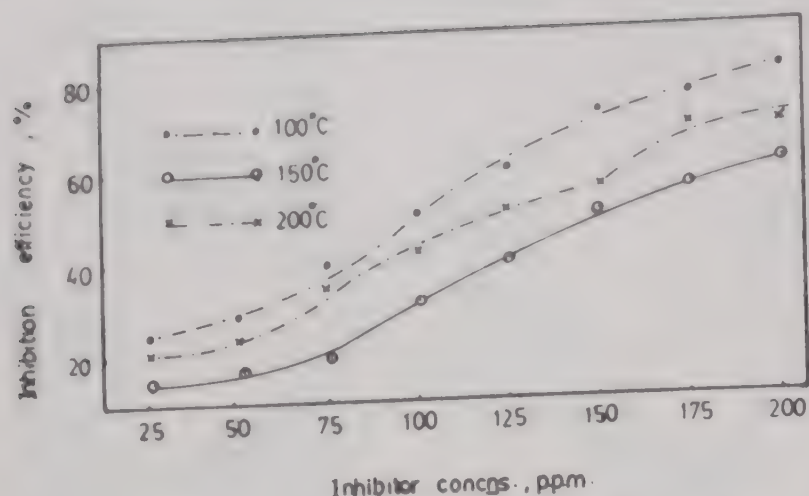


Fig. 5—Effect of ammonia (7 p.p.m) and chlorinated hexadecylamine on corrosion of C-steel

efficiency decreased with increasing temperatures. The temperature is an important factor and it has a profound effect not only on corrosion rate but also it influences the chemical nature of the corrosion inhibitors used in refining operations.

Fig. 6 shows the effect of benzyl and naphthyl 1,2,4 triazole thione on the corrosion rate of carbon steel. It is clear that the triazoles are capable of developing a fair degree of corrosion inhibition at higher concentrations (200 ppm). They consist of one or more polar groups of nitrogen and sulphur which are attached to the metal surface by chemisorption or electrostatic forces.

The benzyl triazole is more effective than naphthyl at all concentrations. This is due to the complex formed between the inhibitor and the metal or the corrosion products formed are unstable.

Fig. 6 illustrates that the two triazol thione inhibitors provide reasonable inhibition at the lowest temperatures but this behaviour was sharply impaired at higher temperatures. This is due to the fact that organic compounds containing sulphur, decomposed in the oil phase tend to provide a more corrosive condition.

The inhibitive efficiency amounted to 95% and 90% for benzyl and naphthyl respectively at (200 ppm).

### Conclusion

The corrosivities of C-steel metal in the vapour phase is higher than those in the liquid phase.  $H_2S$  is not the only corrodant present, HCl and volatile acids are other important factors. It is appeared that metal chloride in the chemisorbed film actually inhibits the reaction of hydrogen sulphide or active sulphur compounds with  $H_2S$  and some volatile acids

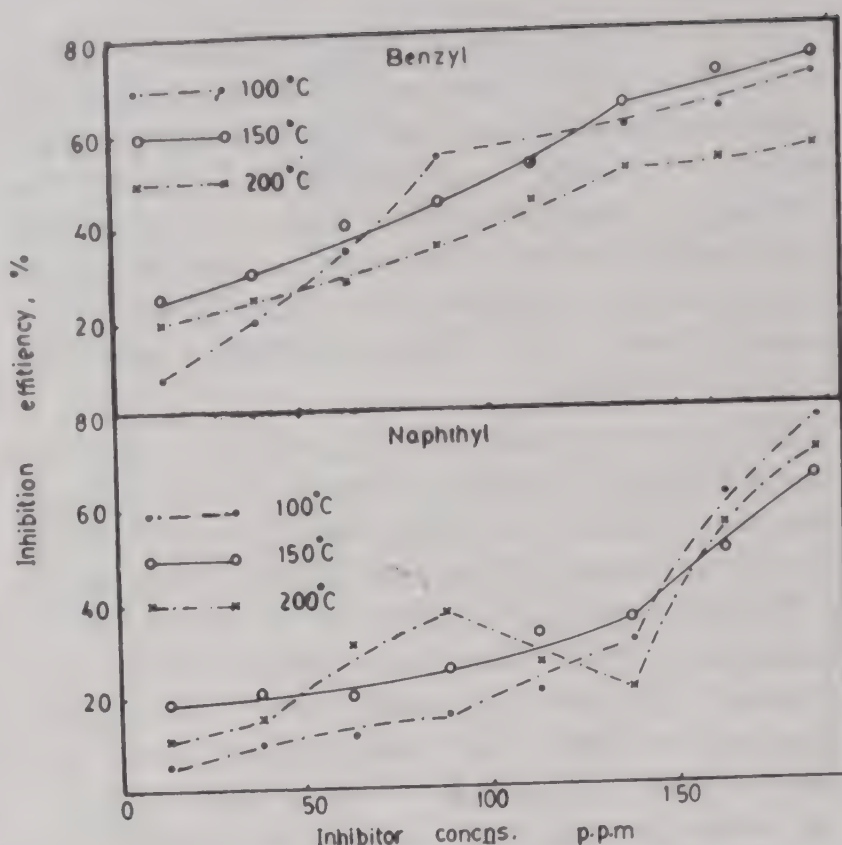


Fig. 6—Effect of triazole 3 thione on corrosion of C-steel

produce strongly acidic solution which is highly corrosive.

It is found that at higher temperature the effectiveness of ammonia decreases as the crystalline salt  $NH_4Cl$  is formed. The rate of inhibition increases with addition of chlorinated hexadecylamine as compared with that obtained by addition of ammonia alone. The anchoring points of the chlorinated hexadecylamine would appear to be the positions of the nitrogen atom in the amino group and the chlorine atom in the alkyl chain.

The benzyl triazole is more effective than naphthyl one and the two inhibitors are capable of developing of corrosion inhibition over the temperature range.

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## Removal of oxalic acid from industrial effluents by using a low-cost material

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A new low cost material is used in the present investigation in removing oxalic acid from its dilute aqueous solutions. The new material adsorbent used was found to be an efficient one and is capable of removing the oxalic acid from its dilute aqueous solutions to the extent of more than 50 per cent and also other toxic pollutants. The process of removal is simple adsorption by contact and is dependent on sorbate as well sorbent concentration besides also depending on the temperature of operation of the process. The new low cost material, thus, gives further scope of its utilisation as an adsorbent for removal of other toxic substances.

In any developing country like ours the discharges of organic and inorganic impurities in industrial waste water is common. The organic impurities like carboxylic acids, phenols, alcohols and amines are not removed by conventional methods used for waste water treatment, as a result they pose variety of environmental problems like odour, toxicity, foaming and colour. Different techniques and methods are presently employed in removing these impurities from waste waters like precipitations, adsorption, floatation, absorption etc of these techniques adsorption was found to be the most promising among the currently known methods. The present study has been made with a view to provide a cheap method for treatment of rubber industry effluents containing carboxylic acids by employing a new low cost material which was found to be an efficient binder for these acids and hence removing them partially or completely depending upon their concentration and the dose of adsorbent. In our earlier investigations the same Low Cost Material has been tested successfully for removal of toxic industrial effluents<sup>1-5</sup>.

### Materials and Method

The paddy straw procured from the fodder shop of local market is cut to the size about 1 cm length, soaked in water overnight and freed from any coloured impurities by repeatedly washing with water and air dried. The dry and clean straw was then sieved and portion retained in between the sieve size of ASTM-7 to 10 was retained as a material adsorbent in the present process.

Test solution of oxalic acid were prepared in different concentrations ranging from 0.2 to 0.02 N

and 100 ml of each of this solution was treated with straw differently as follows.

#### Experiment No. 1

100 ml solutions of oxalic acid of concentration 0.02 N were each treated with different amounts of adsorbent straw, ranging from 0.5 to 7.0 g and equilibrated for a contact time of 24 hours. The residual acid concentrations were measured by conventional methods.

#### Experiment No. 2

100 ml solutions of oxalic acid of different concentrations ranging from 0.02 N to 0.2 N were each treated with 4 g of straw and equilibrated for a contact time of 24 hours. The residual acid concentration was measured in each case by conventional methods.

#### Experiment No. 3

100 ml solutions of oxalic acid of concentrations 0.05 N, 0.1 N and 0.2 N were each treated with 4 g of straw and equilibrated for different time intervals with a fixed stirring time of 10 minutes. The residual concentrations after the lapse of these time intervals were measured.

#### Experiment No. 4

100 ml solutions of oxalic acid of 0.02 N concentration were each treated with 4 g of straw and equilibrated for different time intervals at three different temperatures of 40°C, 60°C and 80°C in shaker bath. The residual concentration after different time intervals were measured as usual for the three different temperatures.

\* For correspondence



## Experiment No. 5

100 ml solution of 0.1 N Oxalic Acid concentration was treated with 4 g of straw and equilibrated with stirring time for a period of one hour with intermittent drawal of sample from the flask at 15 minutes, 30 minutes for measurement of Acid concentration, thereafter the contents were filtered and the acid concentration in the filtrate was measured. The filtered sorbate and sorbent were remixed after a period of one hour and stirred for further period of one hour with intermittent drawal of samples of acid for analysis.

## Experiment No. 6

100 ml solution of Oxalic acid of 0.02 N concentration was treated with 4 g of straw and kept for a contact time of 24 hours. The contents of the flask was then filtered and separated. The filtered adsorbent was then retreated with 100 ml of water and kept for a contact time of 24 hours. The residual acid concentration was measured.

All analytical grade chemicals were used in the investigation. The study was carried out at room temperature of  $38 \pm 2^\circ\text{C}$ .

## Results and Discussion

The results obtained from various adsorption experiments conducted on dilute aqueous oxalic acid solutions with straw as an adsorbent are interpreted in the light of various adsorption isotherms and adsorption equations. These interpretations are as follows:

(1) *Equilibrium Isotherm*

## (a) Effect of adsorbent-Fig. 1

The adsorption of oxalic acid solution of a fixed concentration on different amounts of adsorbent is shown graphically by plotting the amount of acid adsorbed with different amounts of adsorbents in Fig. 1. We conclude from the graph that the variation of adsorption of oxalic acid on straw of different concentration is increasingly uniform upto and adsorbent dose of 4 g. Thereafter no further increase was observed indicating the attainment of equilibrium adsorption at this point.

## (b) Effect of adsorbate Fig. 2

The variation of amount of acid adsorbed with initial acid concentration results in a linear curve, indicating a uniform increase in adsorption with increasing dose of acid for a fixed adsorbent dose of 4 g. No break in the linear curve indicates the adsorbent material has not reached the saturation adsorption

for 4 g of straw upto initial acid concentration of 0.2 N.

## (ii) Langmuir's Isotherm Fig. 3

A linear variation of amount of acid adsorbed with equilibrium concentration for adsorbent dose of 4 gms, indicates the applicability of Langmuir's Isotherm<sup>6</sup>.

$$X/M = KC^{1/n} \quad \dots (1)$$

Besides the linearity in variation also indicates the monolayer nature of adsorption. The values of K and  $1/n$  for the above equation were calculated from the intercept and the slope of the curve and were found to be 1.24 and 0.075 respectively.

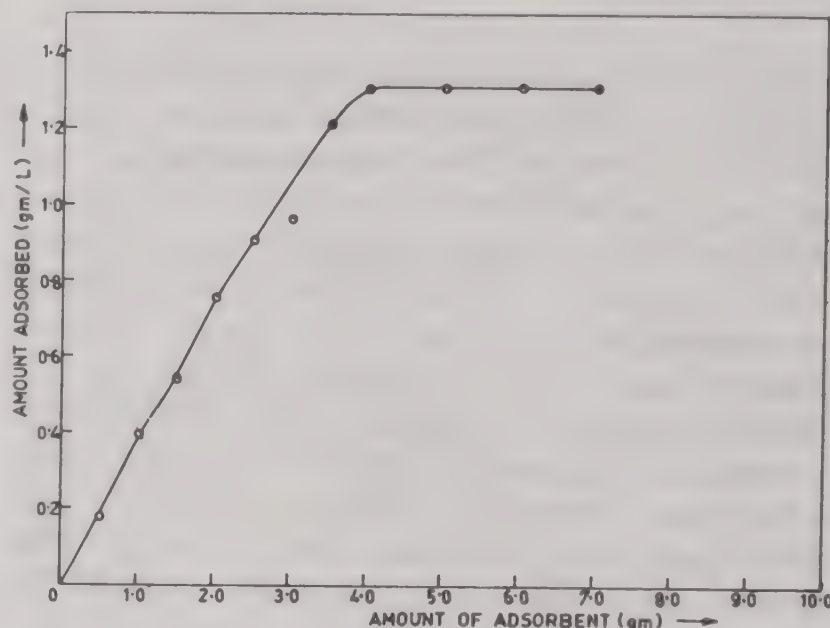


Fig. 1—Variation of amount of acid adsorbed with adsorbent concentration

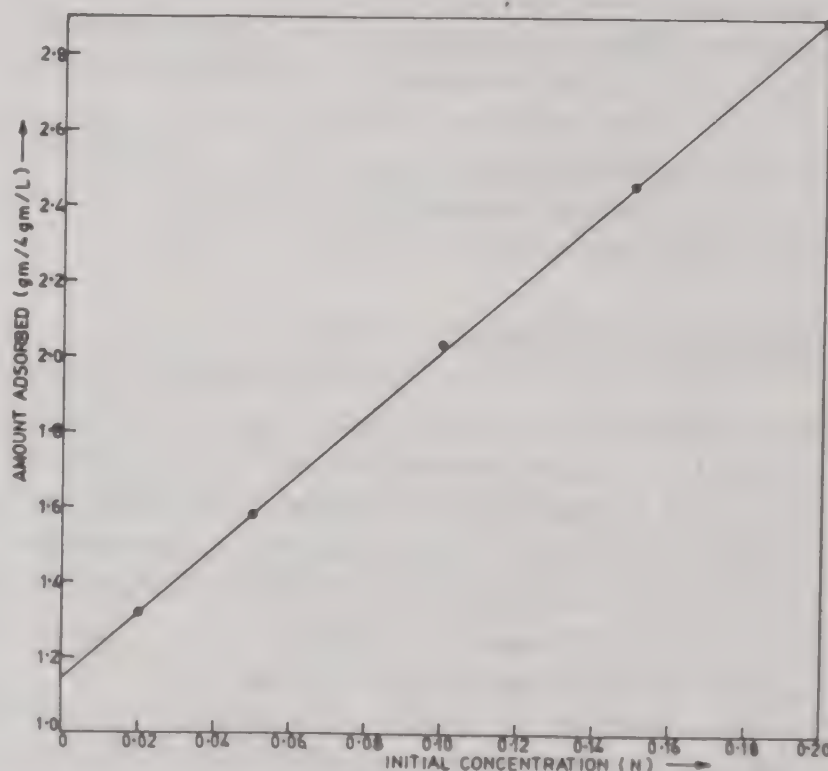


Fig. 2—Variation of amount adsorbed with initial acid concentration



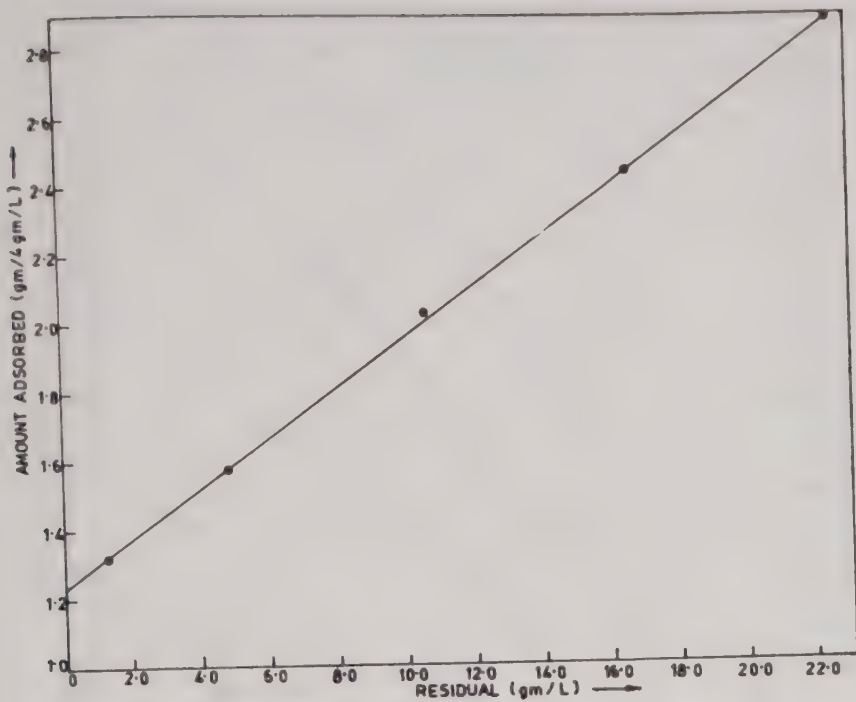


Fig. 3—Saturation curve for oxalic acid adsorption

#### Adsorption Kinetics—Fig. 4

Kinetics of adsorption of oxalic acid on to the surface of straw is studied from the variation of amount of acid adsorbed with time for solutions of acid of three different concentrations and for a fixed adsorbent dose of 4 g. This is represented in Fig. 4. From the figure we observe the adsorption of acid on fixed amount of straw increases with increase in acid concentration with time, and all the three concentrations reaching an equilibrium maxima after a lapse of 120 mts simultaneously. The adsorption equilibrium appears to be directly proportional to initial acid concentration.

The concentration of the acids acts as the driving force accounting for the increased adsorption.

#### Rate constant study Fig. 5

The rate constant for the adsorption of oxalic acid on to the surface of the straw was studied in the light of Lagergren's equation<sup>7</sup>

$$\log (q_e - q) = \log q_e - (K_{ad}/2.303 \times t) \quad \dots (2)$$

$q_e$  = Amount acid adsorbed at equilibrium  
 $q$  = Amount acid adsorbed at time  $t$

The variation of  $\log (q_e - q)$  with time ( $t$ ) resulted in a linear curve representing the applicability of the Lagergren's equation thereby the first order nature of

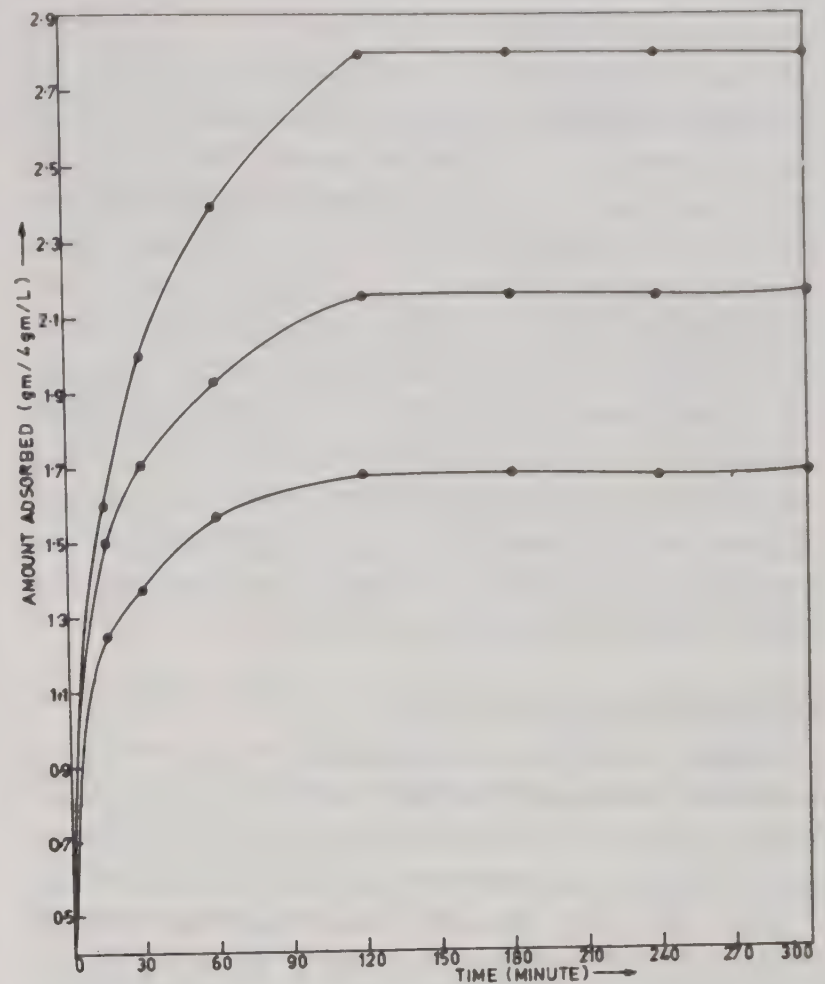


Fig. 4—Variation of amount of acid adsorbed with time

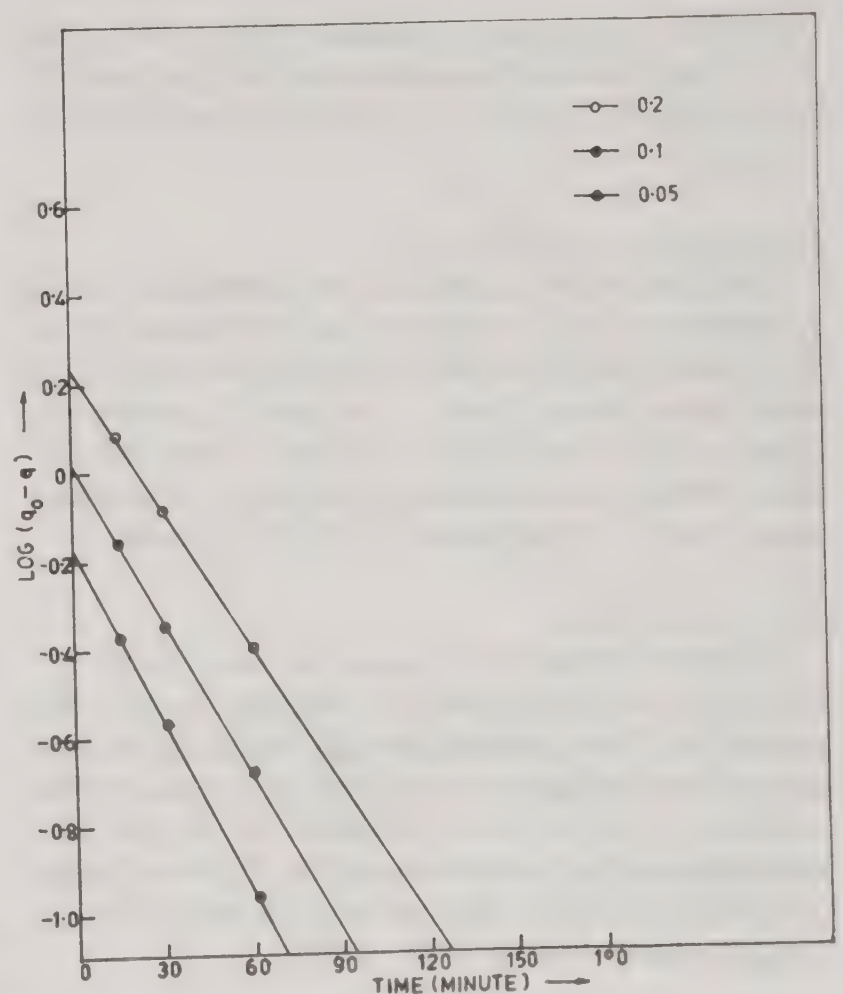


Fig. 5—Lagergren plot for the adsorption rate of the oxalic acid on straw

Table 1—Adsorption kinetic parameters at different concentrations

Concentration (N)	$K_{ad}$ ( $\text{Min}^{-1}$ )	$K_p$ ( $\text{Min}^{-1/2}$ )
0.05	$1.30 \times 10^{-2}$	$8.24 \times 10^{-2}$
0.10	$1.13 \times 10^{-2}$	$11.16 \times 10^{-2}$
0.20	$1.06 \times 10^{-2}$	$14.68 \times 10^{-2}$

the curve. The value of equilibrium rate constant  $K_{ad}$  was calculated from the slope of the above curves and are recorded in Table 1.



### Intraparticle Diffusion study Fig. 6

In any rapidly stirred process the existence of intraparticle diffusion cannot be overruled, besides the adsorption at the outer surface of the adsorbent which are often the limiting steps. This possibility is exploited by plotting the amount of acid adsorbed with squareroot of time ( $\sqrt{t}$ ). A linear curve was obtained for the adsorption process under study indicating the existence of intraparticle<sup>8</sup> diffusion in the process under study. The intraparticle diffusion rate constant  $K_p$  is calculated from the slope of such curves and are recorded in Table 1. The extrapolation of these curves gives further information about the boundary layer affect, i.e. larger the intercept, the bigger is the boundary layer effect<sup>9</sup>.

### Effect of Temperature Fig. 7

To know the effect of temperature on adsorption of oxalic acid on straws, the same was studied for acid of fixed concentration and with same amount of straw at three different temperatures of 40°, 60° and 80°C.

The variation of amount of acid adsorbed in straw with time at different temperature is shown in Fig. 7. We conclude the following from the study of these curve:

- (i) The equilibrium is attained sharply with time
- (ii) Adsorption of acid decreases with increase in temperature indicating the exothermic nature of the process.

### Interruption study Fig. 8

Batch Interruption studies were carried out for the present investigation process and are indicated in Fig. 8 the variation of the amount of acid adsorbed with time. Since there is enhanced adsorption observed after interruption of the process for one hour. Hence, we conclude the process of adsorption under study is dominated by film<sup>10</sup> diffusion.

### Desorption Study

In order to know the nature of adsorption i.e., physical, chemical or both, the desorption study was carried out, the regeneration study could not be done since the adsorbate is an acid. The desorption of the adsorbed acid on straw resulted in 10 per cent desorption of the adsorbed acid back to the solution. Thereby indicating the process of adsorption is predominantly chemical in nature.

Amount adsorbed = 1.46 g/lit.

Amount desorbed = 0.15 g/lit.

### Conclusion

We arrive at the following conclusion from our adsorption experiment with new low cost material

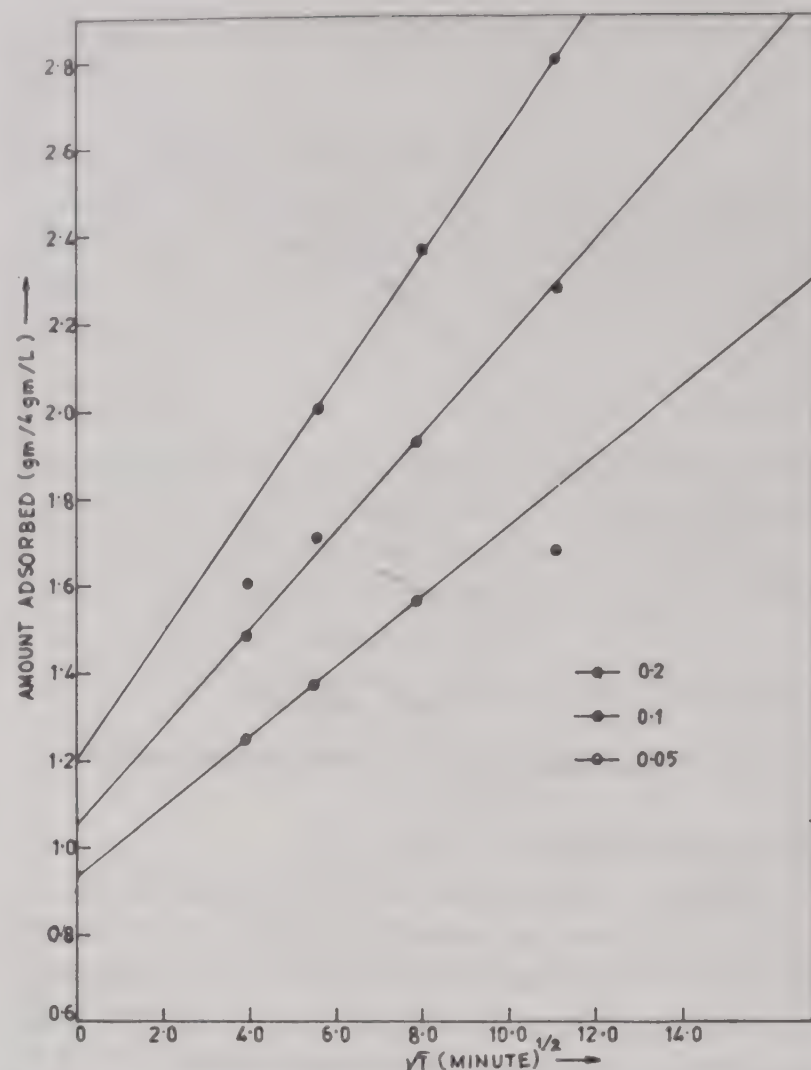


Fig. 6—Intraparticle diffusion plots for the adsorption of oxalic acid on straw

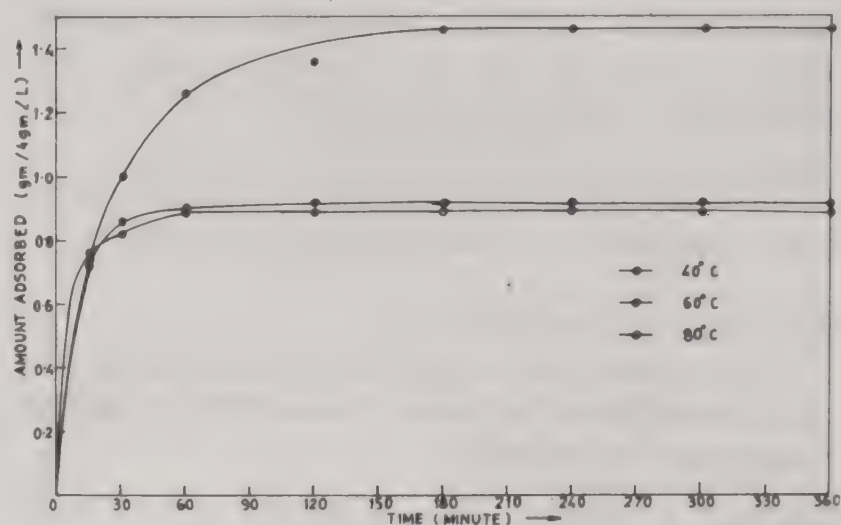


Fig. 7—Variation of amount of acid adsorbed with temperature

- (i) The material is cheap and easily available and is an efficient binder of the acids.
- (ii) The process is dependent of temperature.
- (iii) The adsorbent material poses no problem of disposal as after adsorption it can easily be burnt off getting rid of both adsorbate and adsorbent.

### Acknowledgement

The authors are thankful to Prof. S. Misra, Principal, Regional Engineering College, Rourkela for his encouragement and permitting the use of laboratory to carry out this work.



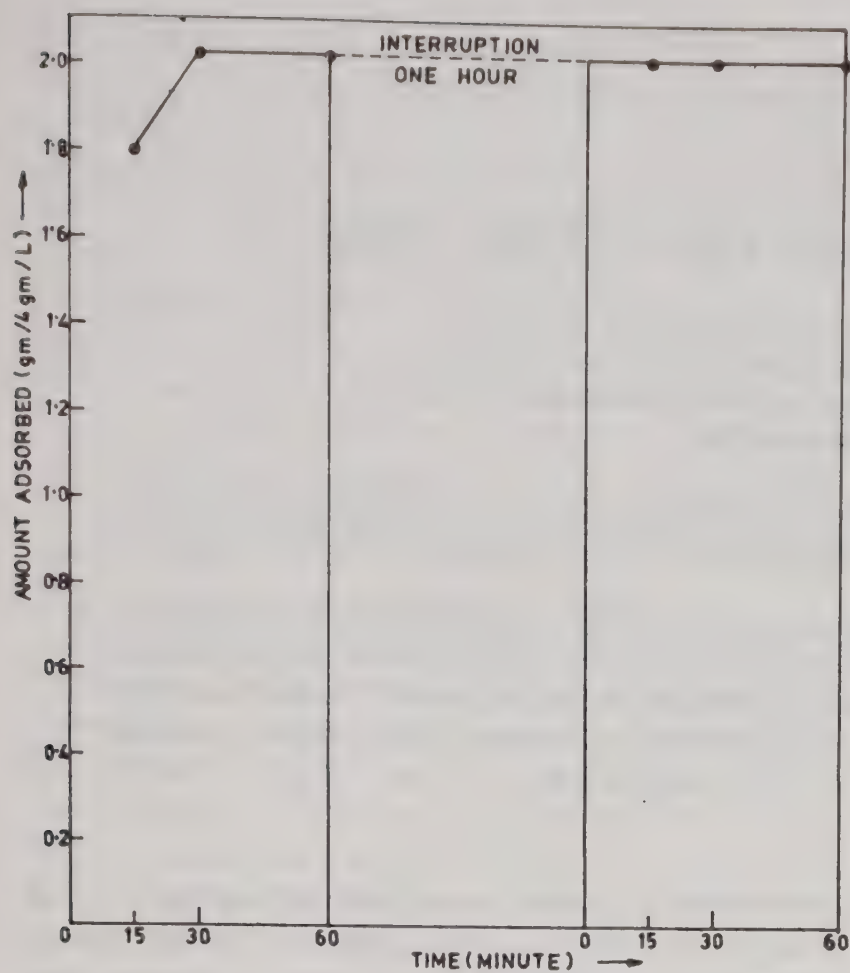


Fig. 8—Interruption test for oxalic acid

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## Behaviour of polyacrylamide encapsulated urease

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Urease (Urea amidohydrolase, EC 3.5.1.5) prepared from Indian jackbean meal has been entrapped in the lattices of polyacrylamide gel. The optimum pH was observed to be 7.0 for both the column as well as batch reactors.

$K_m$  values were found out to be 0.025 M for soluble urease and 0.0245 M for immobilized urease. Energy of activation for the reaction in the presence of immobilized urease was 6.09 Kcal/mole and that for soluble urease was 9.15 Kcal/mole. Optimum protein to gel ratio for the maximum entrapment of urease was 0.16 g protein per 100 gm of polyacrylamide gel. Half-life for the immobilized urease kept at 15°C was 45 days and for the continuous operation of the enzyme reactor at 30°C was 20 days.

Both the inorganic and organic supports are used for the preparation of immobilized enzymes. Generally, the physical adsorption of enzyme molecules onto either inert carriers or ion-exchange resins cannot produce a truly insoluble enzyme as it may be eluted from the adsorbent by changing the ionic strength, pH or temperature. The covalent linkage of protein to insoluble carriers offers a more reliable method of insolubilization, provided the covalent linkages formed are not broken under the reactions. It is generally difficult to find site directed chemical reagents to avoid the probability of bond formation which leads to denaturation of enzyme molecule. Porous glass has been extensively used for immobilizing urease using amino alkylation and diazotization as activation procedures<sup>1</sup>. However it is expensive and not available at commercial scale. Bentonite is also used for immobilization of urease<sup>2</sup>. Preferably, a more general method such as entrapment or encapsulation should be pursued. Bernfeld and Wan<sup>3</sup> have described a method to entrap soluble antigens or enzymes in the lattices of an insoluble highly crosslinked synthetic polymer. Enzymic methods are being used increasingly as analytical tools, particularly in medicine as these methods offer the advantage of overcoming the interference from the proteins present in the solution to be analysed, a state of affairs that often create problems in conventional enzyme analysis, which can be avoided when the enzyme is securely held within a gel matrix. Therefore urease was selected for

entrapment in the lattices of polyacrylamide gel and study its potential as urea analyser. The kinetics of immobilized urease has been worked out. Subsequently the behaviour of polyacrylamide entrapped urease was studied both in batch and column reactor.

### Materials and Methods

Acrylamide, S.D. Fine Chemicals, India  
Bisacrylamide, Loba-Chemie India  
Potassium persulfate, Loba-Chemie India  
TEMED, Loba-Chemie India

All other chemicals used were of analytical grade.

### Preparation of Urease

Urease was extracted from the meal prepared from the dehusked seeds of *Canavalia ensiformis* (jackbean) with 0.1 M citrate buffer (pH 6.0). The enzyme was recrystallized by Dounce's method<sup>4</sup>.

Specific activity of the enzyme varied between 140-190 u/mg of protein at 30 degree C. One unit of urease activity is defined as the amount of enzyme which liberate one micro mole of ammonia per minute at room temperature.

### Preparation of Polyacrylamide Beads and Urease Immobilization

The stock solutions were prepared by dissolving 28 grams of acrylamide in 100 ml distilled water and adding 0.735 grams of crosslinking agents N-N' methylene bis acrylamide (bis) in the same solution. A typical catalyst was prepared by mixing 25 ml of acrylamide solution with 65.8 ml of once

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recrystallized urease having specific activity 190 u/mg. The pH of acrylamide solution was adjusted to 9.5 before the addition of enzyme. To the same mixture 0.12 g of potassium persulfate and 0.12 ml of N-N N'N' tetramethylene diamine (TEMED) were added to catalyse polymerization. Then the enzyme-gel complex was kept at 10 degree C for one hour and stiff gel was granulated by extruding it through an SS press cylinder with an SS wire net. A total of 4 different polymer preparations varying in total monomer concentrations from 5-16 per cent w/v and crosslinking ratio (weight of crosslinking agent/weight of total monomers) from 2.25 to 20 per cent were prepared and studied as catalysts.

The yield of immobilized activity per unit weight of soluble enzyme introduced before polymerization decreased with increasing amount of crosslinking agents. Increasing the total monomer concentration decreased the relative amount of insolubilized urease activity. Therefore a polymer preparation containing 28 g of acrylamide; 100 ml of water with a 0.735 g Bis was selected for routine use as it produced a catalyst of high relative activity with minimum leakage of entrapped urease.

#### *Determination of Entrapping Efficiency of Immobilized Urease*

Entrapping efficiency of immobilized enzyme was usually determined as it represents the percentage of enzyme recovered in the immobilized forms.

#### *Experimental Equipments*

Two types of reactor units were designed to obtain catalytic activity data for this study. A batch reactor was used to obtain data for soluble and the insoluble urease for time periods upto one hour. Insoluble enzyme utilization times in excess of one hour were more conveniently carried out in a flow microreactor system.

#### *Sampling*

Samples were withdrawn from the batch reactor with 1 ml glass pipette and after appropriate dilution the analysis was carried out in 10 ml glass test tubes.

#### *Batch Reactor*

The extruded granule of polyacrylamide gel urease complex was taken into the reactor and to it substrate solution was added. The water swelled polymer was kept suspended throughout the reacting mixture. The reaction proceeded at room temperature (30° C).

The alkalimetric method of Gorin and Chin<sup>5</sup> using phenolphthalein was employed for estimation of urease activity.

#### *Column Reactor*

The micro reactor system used to study the life of the insoluble urease is diagramed in Fig. 1. The feed was passed with the help of a peristaltic pump. The feed passed through thick walled (1/8 inch, outer diameter) teflon tubing to a 100 ml borosil glass column. Immediately down streams from the glass column the feed can enter the microreactor. The reactor consists of a borosil glass chromatographic column (1.9 cm in diameter and 15 cm long). The catalyst was easily dispersed in the column in the interstitial spaces of the polished glass beads (3 mm diameter). Loss of catalyst was prevented by a wool plug at the bottom of the reactor. For temperature control water from a tap was circulated through the jackets of the reactor. The temperature was maintained within  $\pm 0.2$  degree C.

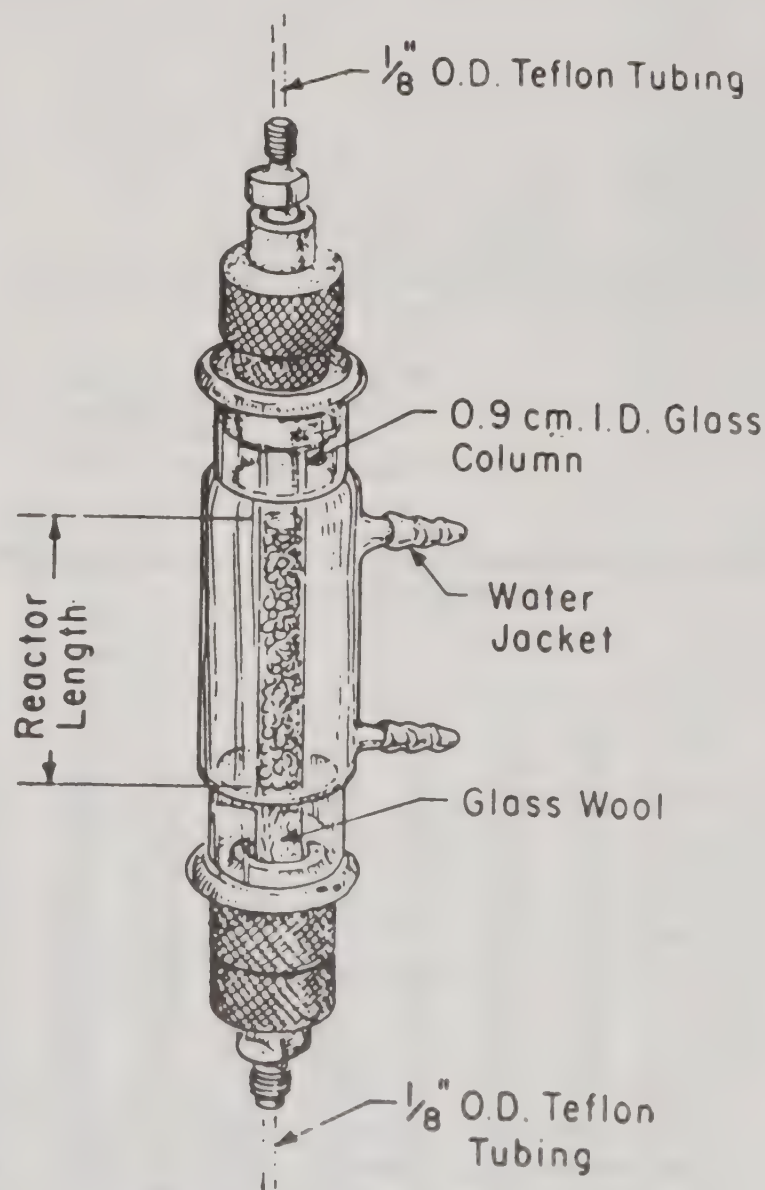


Fig. 1—Microreactor (Column reactor)



A calibration curve was constructed by introducing samples containing various concentrations of urea into the system and measuring the amount of ammonium ion released in the effluent. The sample volume was 2 ml.

Fractions (1 ml) were collected immediately after the introduction of substrate and subsequently determined for released ammonium ions. The result in Fig. 2 shows a good linear relationship between the concentration of urea from 1 mg/ml-10 mg/ml in the sample and the amount of ammonia formed in the effluent. The highest concentration of urea in normal human sera is about 0.4 g/l. Therefore urease immobilized in polyacrylamide can be used for the *in vitro* detection of urea in normal human sera.

Another important factor for a practical column reactor is the reproducibility over a long period. The column was installed in the flow system and an assay was carried out every 60 hours. Between assays the

column was stored with the carrier in a refrigerator at 5 degree C.

#### Characteristics of the Column

Column size (15 cm  $\times$  0.9 cm ID); Urea concentration—0.017 M (1%).

Volume of introduction—2 ml/min.  
Temperature—20  $\pm$  5 degree C.  
Citrate-Phospahte buffer—pH 7.0.

At temperature 20  $\pm$  5 degree C, the activity of immobilized urease column was found to be constant for 20 days. During this period 40 introductions were performed at each temperature (Fig. 3).

#### Determination of Optimum Time of Reaction

The optimum time of reaction of immobilized urease was determined by assaying at different time intervals at 35°C (pH 7.0) using 1% urea as substrate. The results are reported in the Figs 4 and 5.

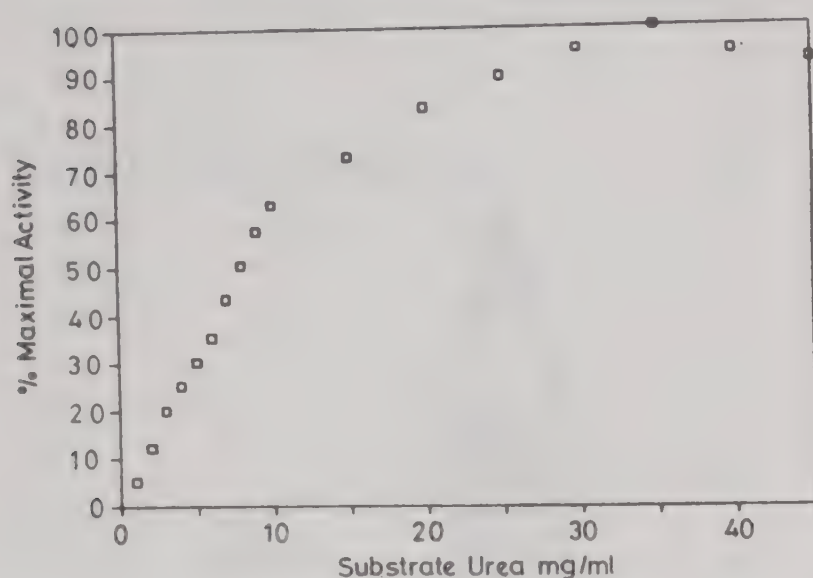


Fig. 2—Determination of optimum substrate concentration for immobilized urease

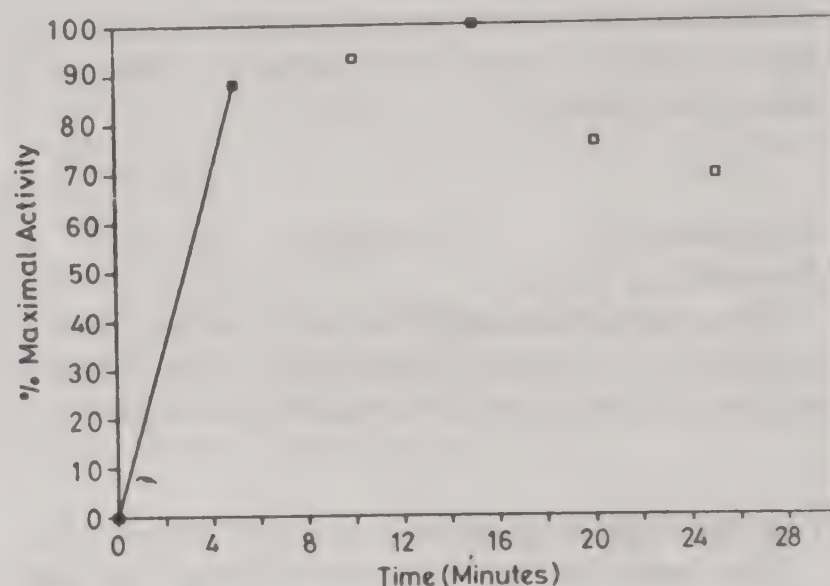


Fig. 4—Optimum time of reaction

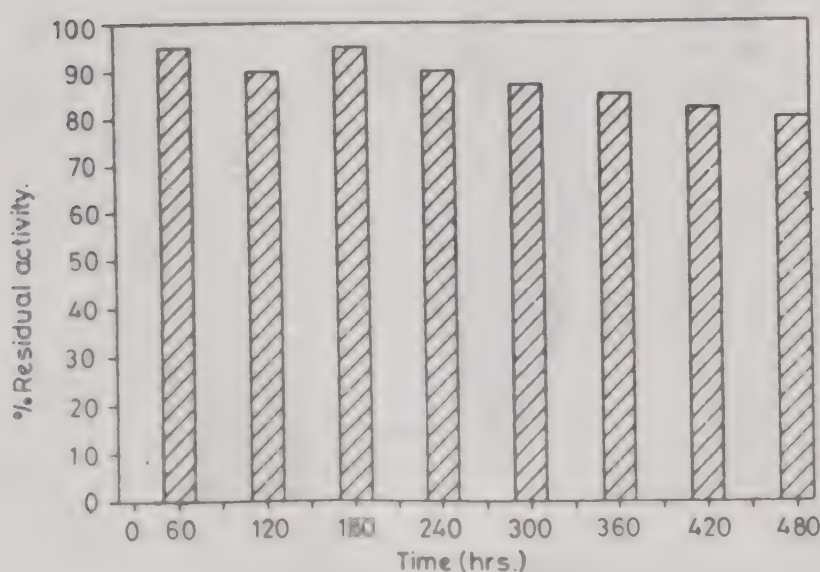


Fig. 3—Stability of immobilized enzyme

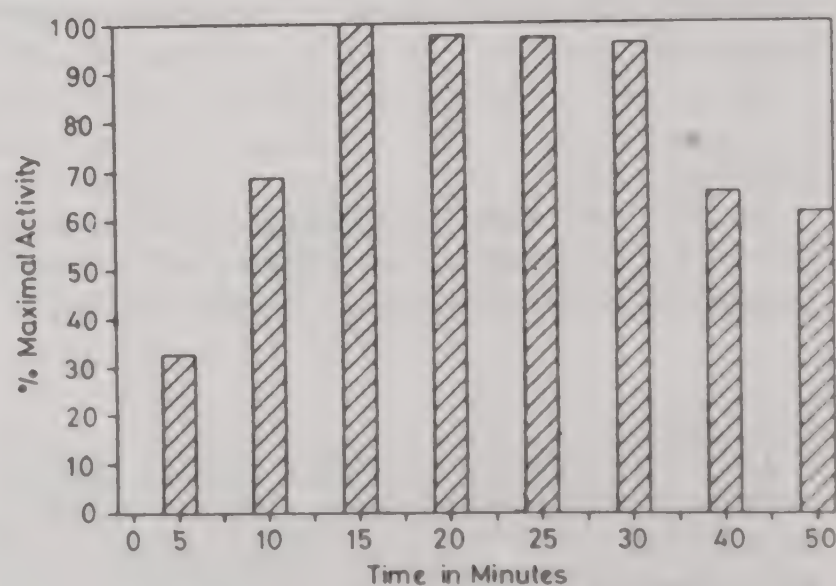


Fig. 5—Optimum time for soluble enzyme



### Effect of pH

The pH optimum for the immobilized urease in batch studies was determined by preparing buffer of required pH (Figs 6 and 7).

### Effect of Protein Loading on immobilization

Immobilization of urease within polyacrylamide gel was carried in the presence of varying initial protein concentration to determine the optimum ratio of gel and protein to achieve the maximum retention of urease activity. Protein was estimated in the supernatant. Immobilized urease was assayed as mentioned earlier. The maximum activity was achieved when 20 mg of urease per 100 ml of gel was used. A further increase in the amount of enzyme did not lead to an increase in the activity. Therefore 20 mg of urease per 100 g of gel was selected for immobilization in the present study. But the actual amount of enzyme immobilized was 16 mg in 100 g gel.

### Effect of Temperature

The immobilized urease was assayed at increasing temperatures (20°-70° C) for determining the optimum temperature. A fresh immobilized urease was used for each assay. An Arrhenius plot was used for the determination of activation energy, the results are reported in the Figs 8,9.

### Heat Stability of Immobilized enzyme

The immobilized urease was subjected to heat stability studies by incubating it for 30 minutes at specified temperatures and then cooled rapidly. Residual activity of the enzyme was determined by the modified Gorin and Chin method<sup>5</sup>.

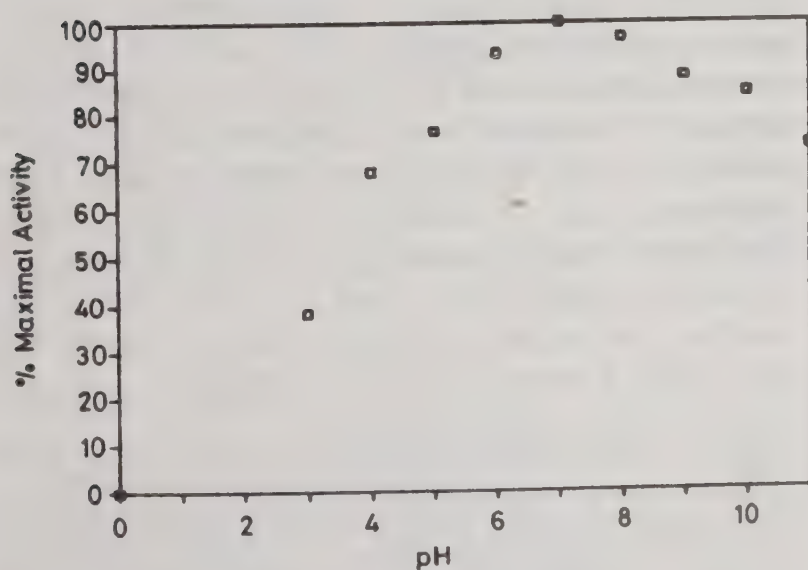


Fig. 6—Optimum pH for immobilized enzyme

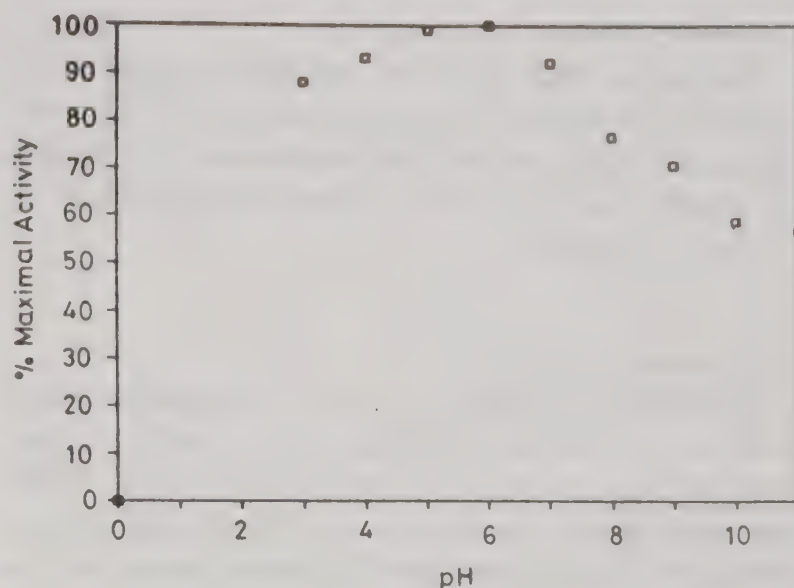


Fig. 7—Optimum pH for soluble enzyme

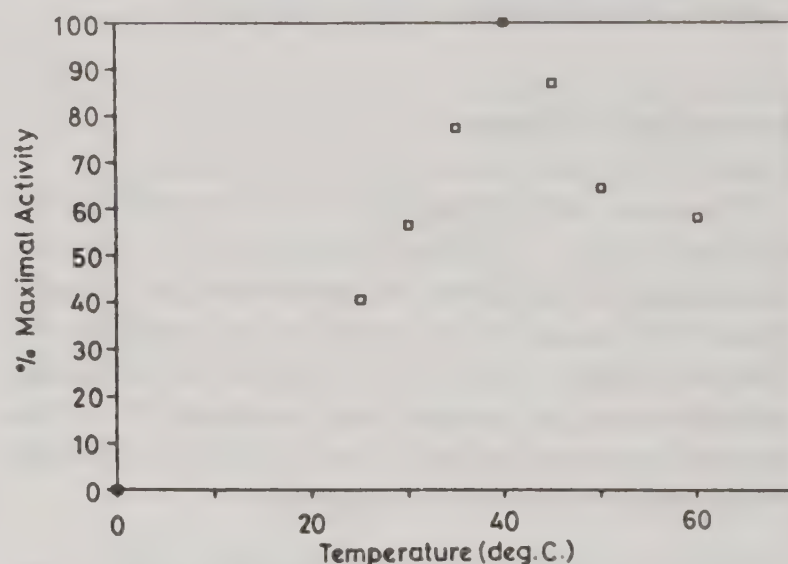


Fig. 8—Determination of optimum temperature of immobilized enzyme

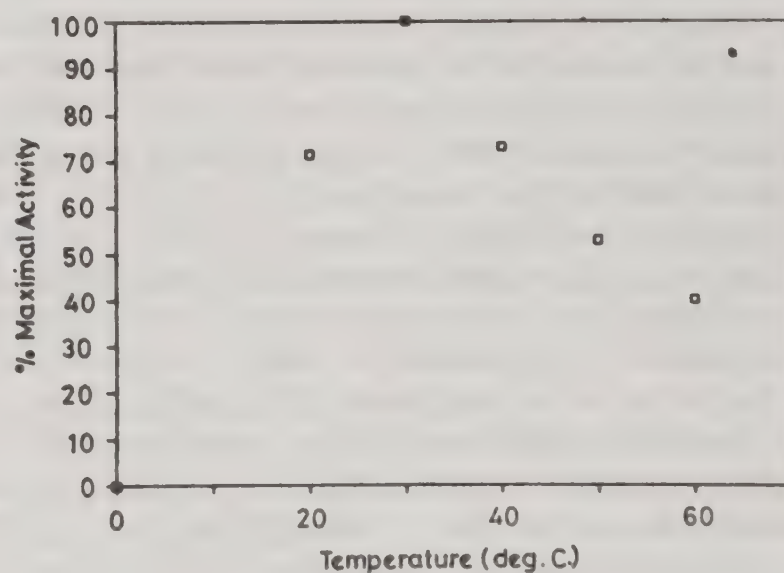


Fig. 9—Optimum temperature: Soluble enzyme

### Effect of Substrate Concentration

The Michaelis-Menten constant ( $K_m$ ) was calculated by immobilized urease by assaying the enzyme at increasing concentrations of urea (M) in batch studies.



### *Storage Stability*

The immobilized urease complex was stored at 15°C and 5°C in citrate-phosphate buffer (pH 7.0) for 45 days and 30 days respectively and during this period the residual activity of the same was determined at various intervals.

### *Operational Stability*

Immobilized urease (1 g) was repeatedly treated with 3 ml of 1% urea solution at pH 7.0 for 15 minutes and the activity was determined every time. Same immobilized enzyme was exposed repeatedly to urea for about 15 times and the retention of the activity is reported.

Protein estimation was done by the method of Lowry, Rosenbrough and Co-workers<sup>6</sup>.

## **Results and Discussion**

### *Nature of polyacrylamide entrapped urease*

The nature of the immobilized enzyme obtained by polymerizing a crosslinked polymer in a solution containing a dissolved macro-molecular enzyme (here in this case, urease) needs to be established so that the relative merits of this type of immobilizing technique can be assessed and applicability of the method can be extended to insolubilization of other commercially important enzymes.

It has been shown by Fishbein and Blakely *et al.*<sup>7,8</sup> that the molecular weight of urease from jackbean is 4,80,000. The co-polymerization of acrylamide and bis in aqueous solution produces a network polymer and the presence of bi-functional agents results in the formation of crosslinkages between the two different chains of the polymer forming in effect, one giant three dimensional macromolecular network<sup>8</sup>. The carboxylic acid-amide groups introduce polarity and the ability to swell in water. The urease prior to the beginning of the polymerization is in an aqueous medium at a temperature at which it is expected to display its native macromolecular configuration. A plausible explanation for the immobilization of urease, is that, the reacting polymer forms, around enzyme molecules encapsulating them in a "cage" like structure with the opening which are on the average, small enough to contain the entrapped enzyme while permitting the passage of lower molecular weight substrate urea. Urease is a rather large protein molecule (M.W 4,83,000) which has a molecular diameter of approximately 125 Å units in its monomeric form<sup>9</sup>. This enzyme is found in a number polymeric forms including a common one called beta urease. This a dimer which has a major

dimension of 250 Å units. Since the substrate is very small with respect to enzyme, the major consideration for immobilizing this enzyme within the pore structure be the major dimension of urease. Previous studies have indicated for optimal stability and loading, that the average pore diameter should be approximately twice the major dimension of the molecule. Thus, if urease is in its monomeric form the optimum pore size should approximate 250 Å unit.

### *Optimum Time of Reaction*

The optimum time of reaction for both soluble and immobilized was reported to be 15-30 minutes and 15 minutes respectively. A lengthening beyond 15 minutes indicated decrease in per cent maximal activity.

### *Effect of pH*

Urease hydrolyzes the substrate urea to form ammonia and carbon dioxide. Both the catalysts showed maximum activity over a pH 6 (soluble) and 7 (immobilized urease) respectively. The initial rate of urea decomposition decreased to 70 per cent of its maximum value that is 100 per cent at pH 11. It has been reported that the optimum pH for the enzymatic reactions of intact urease in solution lies between 6.4 to 7.6, thus optimum pH of immobilized urease remains unchanged<sup>10</sup>.

### *Effect of Temperature and heat Stability of Immobilized Urease*

Reaction temperature was varied from 20°C to 70°C. At low temperatures all the runs obeyed the Arrhenius temperature dependency until a critical temperature was reached, then the initial rate of reactions decreased rapidly with increasing temperature indicating a denaturation of protein molecule. Soluble urease from jackbean has an optimum around 30°C<sup>11</sup>. There is a significant increase in the optimum temperature (40°C) when urease was entrapped in polyacrylamide. Thus indicating that immobilized urease resists denaturation due to temperature. Activation energy of soluble urease was found out to be 9.147 kilo calories per mole and 6.09 kcal per mole for immobilized urease (Figs 10,11,12,13).

Sizer<sup>12</sup> has found the activation of urease-urea system over a temperature range from 0.2-50°C to vary from 8700 to 11,700 Kcal/mole. Activation energy of molecular sieve bound urease was calculated to be 7.4 Kcal/mole<sup>13</sup>.



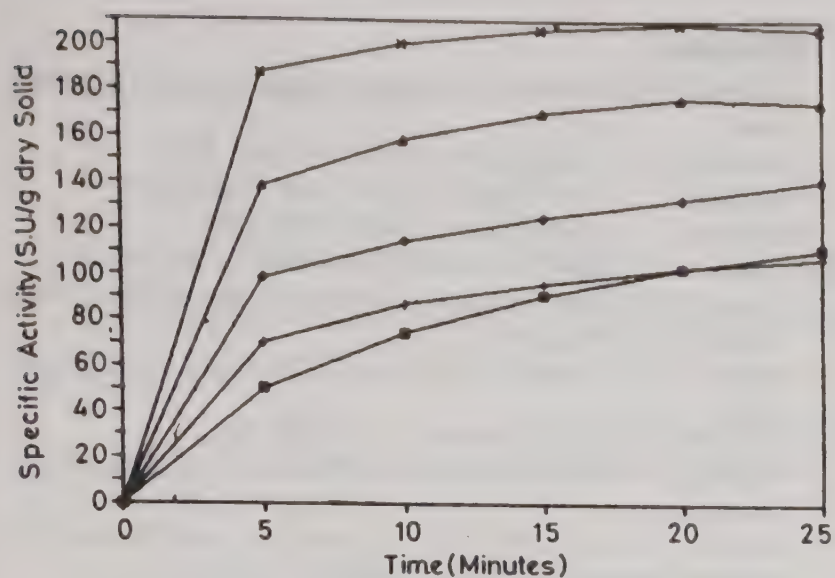


Fig. 10—Activation energy for immobilized enzyme

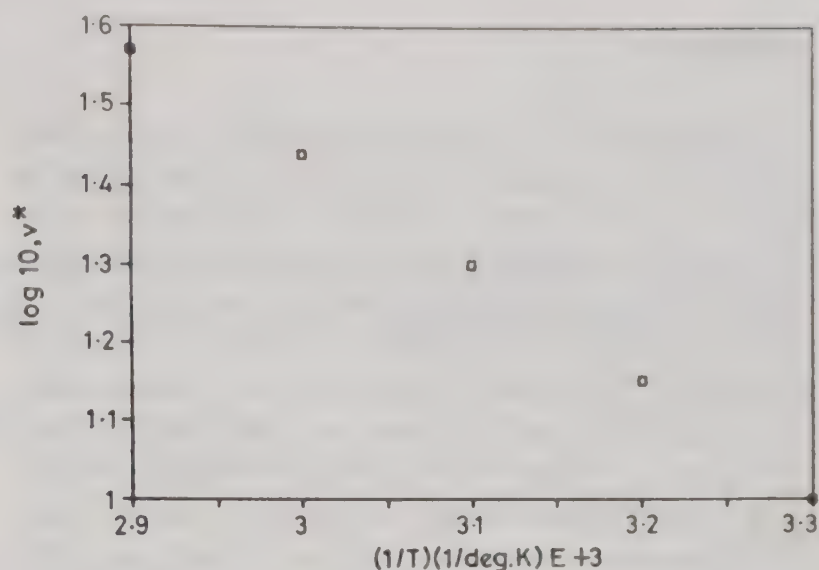


Fig. 11—Activation energy for immobilized enzyme: Arrhenius plot

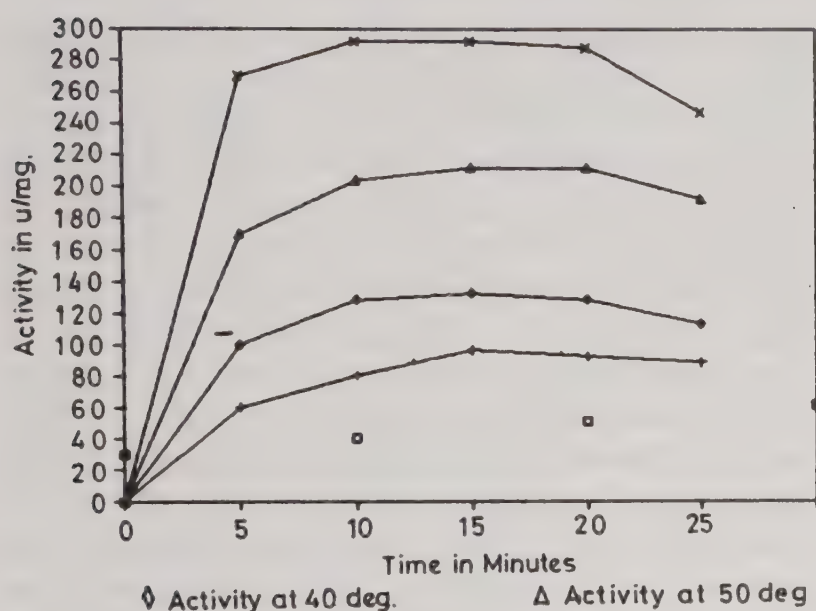


Fig. 12—Activation energy for soluble enzyme with respect to time at diff. T.

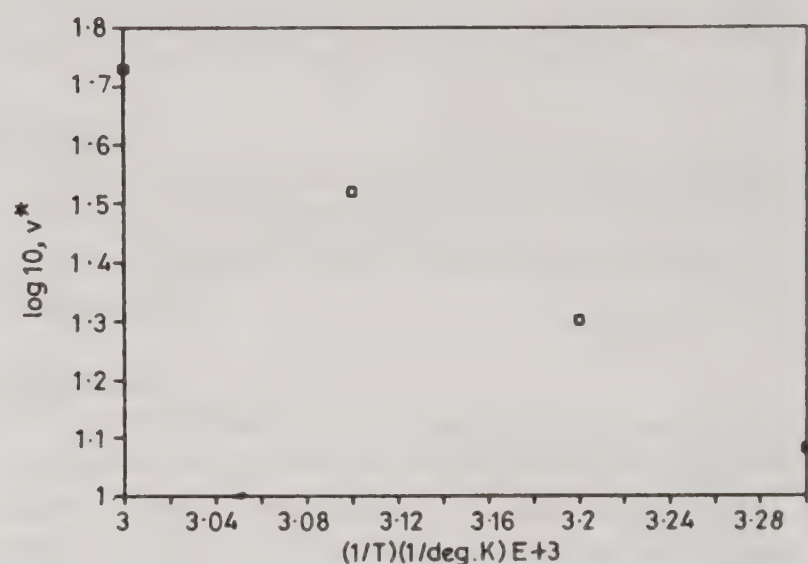


Fig. 13—Activation energy: Data for Arrhenius plot

### Effect of Substrate Concentration and $K_m$ Determination

From the Lineweaver Burk plot the  $K_m$  for the immobilized urease was found out to be 0.024 M whereas, for soluble urease it was found out to be 0.025 M.  $K_m$  for molecular sieve bound urease has been reported to be 0.025 M<sup>13</sup>. Urea exerts inhibition on urease activity. Inhibition was observed beyond 10 mg/ml in our case. Porous glass immobilized urease by Weetal showed inhibition beyond 0.34 M<sup>1</sup>.

### Storage Stability

The activity of polyacrylamide urease complex becomes almost 50 per cent at the end of 45 days in cold citrate-phosphate buffer (pH 7.0) at 15°C and remains almost 100 per cent at the end of 30 days period when stored at 5° C. Therefore it can be inferred that polyacrylamide entrapped urease can be

used in clinical practice for the determination of serum urea. In column reactor the 80 per cent activity was retained upto 480 hrs. Half-life of molecular sieve bound urease at 20° C was calculated to be 35 days<sup>13</sup>.

### Operational Stability

93.91 per cent activity was retained even upto 15 times repeated urea treatment. Column studies showed that activity of polyacrylamide urease insoluble complex remained constant upto 20 days.

Determination of optimum concentration of Acrylamide and Bis:

Weight of monomers is grams per 100 g of

Gel	5.1	7.2	2.5	17.5
Acrylamide	97.5	97.2	80.0	91.0
Bis	2.5	2.5	20.0	9.0
Relative Activity	90.0	100.0	93.0	90.0



## Conclusion

In conclusion the authors would like to add, that immobilized urease enzyme in polyacrylamide matrix would help fertilizer companies and pathologists immensely. One has to just introduce the sample in the reactor and get the analysed product i.e. carbon dioxide and ammonia within a matter of seconds. The fertilizer companies can utilize their waste in recovering the important raw material and reprocess it back to the final product. The pathologists have to keep the reactor ready for use, when a sample comes they just have to sediment the cells, recover the serum and analyse it for the urea determination. Thus this immobilized urease can be handy and a very useful tool.

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## Co-chemical and thin-layer chromatographic characterization of the prepared tincture of *Moringa oleifera* Lam. (Fam. Moringaceae)

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Different strength of alcohol 40, 50, 60, 70, 80, 90% v/v and dehydrated were utilized for the preparation of tincture of *Moringa oleifera* by maceration for 10, 20 and 30 days. 60 per cent alcohol on 30 days of maceration produced maximum yield of total solid and that was characterized by thin-layer chromatography.

*Moringa oleifera* Lam. (Fam. Moringaceae) is well known for its various medicinal properties<sup>1-4</sup>. The present investigation aims to find out the suitable strength of diluted alcohol to prepare the tincture of *M. oleifera*, and to produce the maximum yield of total solids, and to study the possible change of pH during the process, the maximum number of days required for effective maceration, the chemical group tests and the thin-layer chromatographic characterization of the tincture which yielded maximum total solids. These type of experiments have also been carried out in our Department previously as in case of *Eugenia jambolana*<sup>5</sup>, *Avena sativa*, *Carduus marianus*, *Hydrastis canadensis*, *Bryonia alba*, *Embelia ribes* and *Andrographis paniculata*<sup>6</sup>.

### Materials and Methods

Leaves of *Moringa oleifera* Lam. were collected locally and identified in our laboratory<sup>1</sup>. The other materials required are: silica gel G, Kieselgurh G, dehydrated ethanol, vanillin, phosphoric acid, anisaldehyde, sulphuric acid, chloroform, methanol, *n*-propanol, cyclohexane, ethyl acetate, sodium acetate, Dragendorff's reagent. All materials and reagents used are of Analytical Reagent grade. The leaves were dried, powdered and passed through a 60 mesh sieve. Twenty-one ambered coloured bottles were taken, 200 ml of alcohol of following strengths; 40, 50, 60, 70, 80, 90 per cent and dehydrated alcohol were poured in separate three sets of 7 bottles each. Each set of seven bottles was kept for maceration for 10 days, 20 days and 30 days respectively. The materials were filtered through sintered glass crucible (G-4) under reduced pressure.

The physical constant values such as colour, pH, specific gravity, solid matter per 100 ml were studied.

The chemical group tests and thin-layer chromatography of the tincture were performed<sup>7,8</sup>.

### Results

The colours of tinctures are same in the tinctures prepared by 10, 20 and 30 days of maceration. All the tinctures were clear liquid without any turbidity or sedimentation.

### Discussion

The sets of tinctures were prepared by maceration process utilizing multiples of 10 per cent strengths of diluted alcohol and dehydrated alcohol. The products were kept for 10, 20 and 30 days. The effect on the colour, pH and total solid content for the respective days were studied and noted.

The colour of tinctures were varied with different strengths of alcohol. This is due to the variations of the constituents present in them. The colour is same in each set for a particular strength of alcohol (Table 1).

The variations of pH of the tinctures prepared at different days of maceration were quite distinct (Table 2). Such change indicates the variations in total solid content and chemical constituents present in

Table 1—Colour description of the tinctures

% of alcohol (v/v)	Colour of prepared tinctures
40	Brownish black
50	Brownish green
60	Brownish green
70	Light greenish yellow
80	Greenish yellow
90	Green
Dehydrated	Deep green

\*For correspondence



them. This change may also occur due to prolonged contact with glass.

From Table 3, it has been observed that the specific gravity is highest at 60 per cent alcohol in each set.

The total solid content is also maximum at 60 per cent alcohol strength and after 30 days of maceration. Then the solid content is decreased with increase of alcohol strength (Table 4).

The object of such investigation was to find out which strength of diluted alcohol was suitable to extract maximum amount of soluble constituents and the number of days required for effective maceration to bring out maximum amount of soluble constituents.

As 60 per cent alcohol extracts maximum amount of solid content, the chemical group tests is performed of that tincture. Presence of alkaloid, amino acid, sterols, sugars, gums are observed. The characterization of the tincture is performed by thin-layer chromatography (Table 5). Presence of amino acids (Table 5A), sterols (Table 5B), sugars (Table 5C) and alkaloids (Table 5D) are observed.

This study will help to prepare the tincture of *M. oleifera* which has a potential therapeutic value and in homeopathic medicinal world, the tincture of *M. oleifera* will serve a lot to cure several diseases.

Table 2—pH of the tinctures

Alcohol strength (% v/v)	pH (with duration of maceration)		
	10 days	20 days	30 days
40	3.8	4.1	4.2
50	4.1	4.3	4.7
60	4.7	4.9	5.1
70	4.2	4.6	4.8
80	3.6	3.8	3.9
90	3.5	3.9	4.1
Dehydrated	3.8	4.0	4.2

(Each reading is an average of three determinations)

Table 3—Specific gravity of the tinctures

Alcohol strength (% v/v)	Sp. gravity (with duration of maceration)		
	10 days	20 days	30 days
40	0.9222	0.9231	0.9244
50	0.9346	0.9361	0.9372
60	0.9422	0.9432	0.9451
70	0.9216	0.9227	0.923
80	0.8904	0.8917	0.8801
90	0.8840	0.8851	0.8840
Dehydrated	0.8796	0.8802	0.8791

(Each reading is an average of three determinations)

Table 5—Thin-layer chromatographic characteristics of the tincture prepared with 60% alcohol

(A) Stationary phase: Silica gel G

Solvent system: *n*-propanol:water (7:3)

Developing agent = Ninhydrine solution

Room temperature = 31°C

No. of spots	Rf values	Colour after spray
1	0.83	Pink
2	0.77	Pink
3	0.61	Violet
4	0.52	Violet
5	0.46	Violet

(B) Stationary phase: Kieselguhr G

Solvent system: Cyclohexane-ethyl acetate (9:1)

Developing agent: Vanillin-phosphoric acid

Room temperature: 31°C

No. of spots	Rf values	Colour		
		UV light	After spray with vanillin phosphoric acid	I <sub>2</sub> vapour
1	0.91	Bluish-green	Blackish	Deep brown
2	0.32	—	—	Brown

(C) Stationary phase: Silica gel G impregnated with 0.02 M sodium acetate

Solvent system: Chloroform-methanol (6:4)

Developing agent: Modified anisaldehyde-sulphuric acid

Room temperature: 31°C

No. of spots	Rf value	Colour	
		After spray with modified anisaldehyde-sulphuric acid	I <sub>2</sub> vapour
1	0.47	Violet	Deep brown
2	0.36	Green	Brown
3	0.27	Green-grey	Brown

(D) Stationary phase: Silica gel G

Solvent system: Chloroform-ethanol (95%) (9.6:0.4)

Developing agent: Dragendorff's reagent

Room temperature: 31°C

No. of spots	R <sub>f</sub> value	Colour	
		After spray with Dragendorff's reagent	I <sub>2</sub> vapour
1	0.86	Orange-red	Deep brown
2	0.63	—	Brown
3	0.34	—	Brown
4	0.12	—	Brown



Table 4—Solid matter content of the tinctures

Alcohol strength (% v/v)	Solid matter content of the tinctures		
	10 days	20 days	30 days
40	0.9183	0.9193	0.9217
50	1.1921	1.2134	1.2573
60	1.1234	1.3827	1.4829
70	0.6059	0.6093	0.6142
80	0.0627	0.0631	0.0652
90	0.0539	0.0552	0.0574
Dehydrated	0.0346	0.0373	0.0385

(Each reading is an average of three determinations)

### Acknowledgement

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## Effect of nitrogen concentration on hydrodesulfurization

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The effect of the presence of nitrogen compound on hydrodesulfurization (HDS) of a petroleum fraction in the middle distillate range was studied in a batch reactor. Simultaneous HDS and hydrodenitrogenation (HDN) as well as the effect of hydrogen sulfide gas on HDN were also studied. Increasing nitrogen concentration has a detrimental effect on sulfur removal. Nitrogen concentration as low as 0.2 wt% in the feed has negligible inhibiting effect. HDN rate initially increases with increase in the  $H_2S$  partial pressure in the reactor atmosphere but after certain pressure of  $H_2S$  the HDN rate decreases.

Synthetic crudes extracted from oil shale, coals, or certain low-grade naturally occurring petroleum contain large amounts of both sulfur and nitrogen compounds. The concentration of both groups of compounds must be reduced sufficiently to meet air pollution standards and to prevent catalyst poisoning in subsequent hydrorefining operations.

Hydrodesulfurization (HDS) occurs simultaneously with hydrodenitrogenation (HDN), but the interaction between the two are little understood. It has been shown<sup>1,2</sup> that pyridine, a basic nitrogen compound, severely inhibits the hydrodesulfurization of thiophene on sulfided cobalt-molybdate type of catalysts. Significant differences in desulfurization due to nitrogen compounds structure have also been reported<sup>3</sup>. It was stated that the decreasing inhibitor strength with respect to some common nitrogen compounds followed the order : imidazole > quinaldine, quinoline > pyrrole, pyridine > piperidine, indole > decylamine; n-butylamine > aniline. In an experiment with heptane-heptene feed containing about 0.4 wt % sulfur, as thiophene, to which pyridine (up to 0.2 wt % N) was added, it was shown<sup>4</sup> that olefin hydrogenation was more strongly inhibited by nitrogen compounds than hydrodesulfurization. The effect was ascribed to the existence of different catalytic sites for hydrogenation and desulfurization which was more pronounced for sulfided nickel-alumina than for sulfided cobalt molybdate-alumina. It is proposed<sup>5</sup> that the desulfurization occurs on two types of catalytic sites. The first being very active for HDS but very sensitive to nitrogen bases, sufficient quantities of which completely block these sites rendering them inactive for HDS. The second type which were much less active for HDS and also less susceptible to sulfur poisoning were mostly responsible for HDS activity after the first type of sites were blocked.

The purpose of the present work was to examine the effects of varying concentrations of nitrogen compound and to ascertain the minimum concentration at which nitrogen begins to affect the HDS operation. The possible mechanism for the inhibition reaction has also been discussed. Since most of the previous studies have been carried out using model sulfur and nitrogen compounds the results with actual feed may differ. The present studies, therefore, were undertaken using a petroleum fraction in the middle distillate range as feed.

### Experimental Procedure

Experiments were carried out in a batch, stainless steel reactor of 2-litre capacity with a rocking device. The reactor was heated from outside by placing in a furnace which was electrically operated. The temperature inside the reactor was measured through a thermocouple arrangement and the temperature was controlled within  $\pm 2^\circ\text{C}$ . The effects of parameters like hydrogen pressure, temperature of the reaction, catalyst-to-oil ratio and residence time were examined. After the specified reaction period, the reactor was taken out of the furnace housing, cooled and the products analysed.

The estimation of sulfur in the feed and product samples were done by Lamp Method (ASTM 1266-56T), where as the nitrogen was found through chemical analysis of the ammonia present in the associated gas.

The feed used was a petroleum fraction of following specifications

Boiling range	250-370°C
Sp. gr. at 27°C	850 Kg/m <sup>3</sup>
Sulfur content	0.78% by wt.
Viscosity	5 centistokes at 37.8°C
Pour point	6°C



Pyridine in different proportions (0.00 to 1.0 wt%) was added to the feed as nitrogen source.

The hydrogen with > 99.5% purity was obtained from cylinders.

**Catalyst selection and preparation**—In an earlier study<sup>6</sup> of the hydrodesulfurization of coal liquids, the relative activities of three Ni-Mo, eleven Co-Mo and four Ni-W catalysts were examined. The results indicated Ni-Mo as the most active catalyst followed by Ni-W and Co-Mo in that order. The reasons for the higher activities of Ni-Mo was stated to be higher hydrogenation capability in the sulfided form, high surface areas and pore volumes and significant surface areas and pore volumes in desirable pore size range.

The studies on the catalyst deactivation during hydrotreatment of coal-derived liquids<sup>7</sup> using Ni-Mo and Co-Mo catalysts showed that the Ni-Mo catalyst perform better than Co-Mo. Although both the catalysts indicated a significant loss in their activities for sulfur removal due to the carbonaceous deposits which were said to occur during the initial hours of oil-catalyst contact, the Ni-Mo spent catalysts contained less carbon compared to the Co-Mo catalysts. This phenomena was stated to be due to the better hydrogenation power of nickel compared to the cobalt in the catalyst. The surface areas of the Ni-Mo/alumina spent catalysts were observed to be less than half of the surface area of the fresh catalyst. In the case of Co-Mo/alumina catalyst, greater reduction on surface area was observed even though these were in contact with the oil for less period of time than the Ni-Mo/alumina catalysts.

For the present studies, therefore, Ni-Mo supported on alumina was chosen as catalyst for the HDS operation.

Supported Ni-Mo catalyst was prepared by co-impregnation of the solution of ammonium paramolybdate and nickel nitrate on alumina at 80°C. The solutions contained the calculated amounts of salts so as to give a final composition of NiO 5%, MoO 12% on alumina. The slurry thus obtained was thoroughly agitated for 15 min. and then evaporated to dryness in an oven at 120°C. The dried powder was calcined at 550°C under a constant flow of air for about 5 hr. The catalyst was then pelletized and used in the size range of -10 to +14 mesh after presulfiding *in situ* in the calcination furnace. Fresh presulfided catalyst was used in each run.

## Results and Discussion

The results obtained in the present work refer to the batch experiments with following operating conditions: temperature 300 to 450°C, total pressure 2.0 to 3.1 MPa, catalyst/oil ratio 0.65 and residence time 15 to 60 minutes. Studies were made with the feed (total sulfur content, 0.78 wt%) doctored with pyridine at varying nitrogen concentrations of 0.20, 0.25, 0.5, 0.7 and 1.0 wt%.

At a fixed operating condition, the reactions were carried out using feed with different concentration levels of nitrogen. With the increase in nitrogen amount in the feed, the extent of HDS was found to decrease. This decrease in HDS in turn generated lesser amounts of H<sub>2</sub>S (which remains in the surrounding atmosphere). Therefore, with the same experiments, the effect of varying concentrations of H<sub>2</sub>S on HDN could also be simultaneously studied.

**Effect of nitrogen concentration on HDS**—The results of varying concentrations of nitrogen on HDS have been shown in Fig. 1. It may be observed that the per cent HDS decreases with the increase in the amount of nitrogen in the feed. At a fixed operating condition of 390°C temperature, 2.75 MPa pressure and 30 min. reaction time the per cent HDS was found

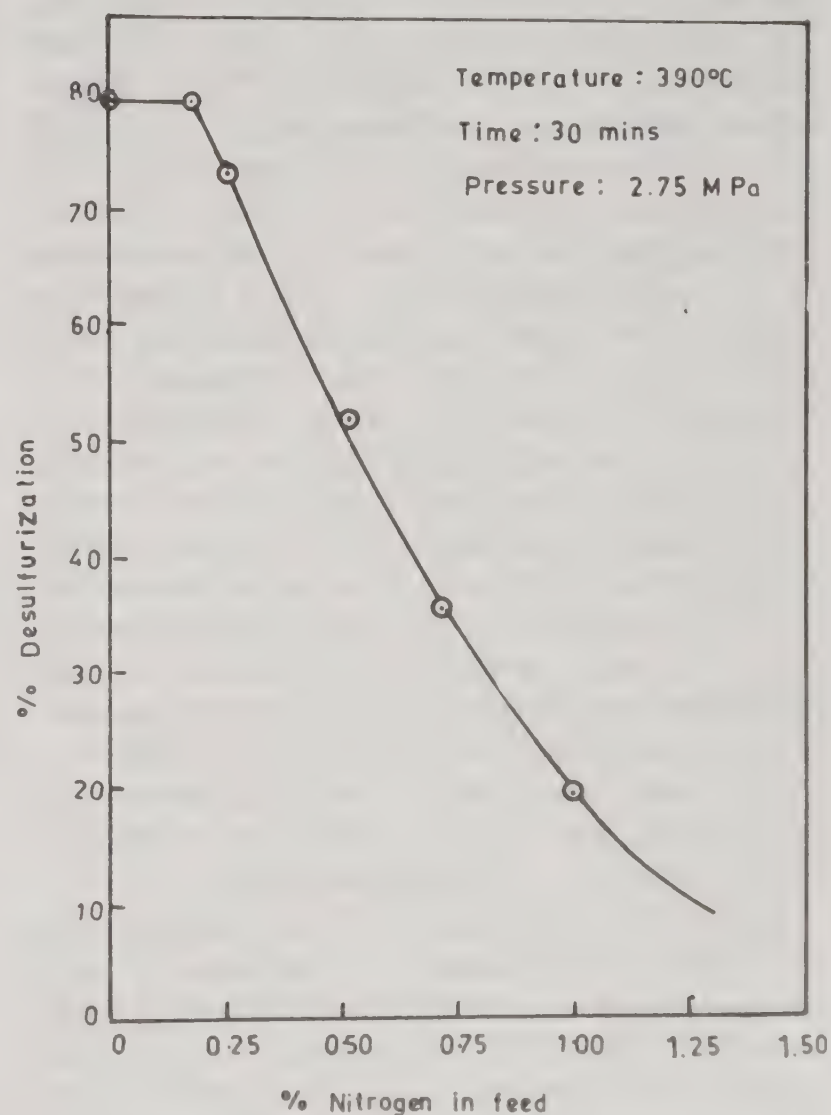


Fig 1—Effect of nitrogen concentration on % hydrodesulfurization



to decrease from 79.33% at zero nitrogen concentration to 51.6% at 5 wt% nitrogen concentration and finally to 19.2% HDS activity at 1.0 wt% nitrogen in the feed.

Previous studies on simultaneous HDS/HDN also indicate a similar behaviour of nitrogen compounds inhibiting the HDS process<sup>4,8-10</sup>. The studies using pure compounds<sup>10</sup> reveal that pyridine poisoned thiophene HDS on a presulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in a manner indicating that there were two sites which have HDS activity. Pyridine apparently poisons these sites to different extents.

In an attempt to further explain this phenomena some studies were made<sup>3</sup> on the behaviour of various types of nitrogen compounds on HDS activity. The nitrogen compounds included several alkyipyridines 2,5-dimethylpyrrole 4-methylaniline, and benzylamine. It was shown that the addition of equimolar (equivalent to 100 ppm of nitrogen) quantities of three alkyipyridines to the base feed resulted in inhibition of desulfurization to widely different extents. Severe inhibition was observed in the case of 4-ethylpyridine while 2,6-dimethyl-pyridine and 2,4,6-trimethylpyridine had no effect. Inhibition by other nitrogen compounds tested fell between these two extremes. The adsorption constants for various nitrogen compounds were also calculated. These studies indicate inhibition of desulfurization is to be clearly related to the structure of the nitrogen compounds. This effect is very clearly shown by alkyipyridines, which suggests that adsorption of pyridine molecule on the active desulfurization site is through the nitrogen atom rather than the aromatic ring. Alkyl groups attached to ring carbons adjacent to the nitrogen atom hinder such adsorption of pyridines. On the contrary, only slight inhibition was obtained with 4-methylaniline, even though the nitrogen in this compound is unhindered. The apparent reduced chemisorption of this compound was explained due to the delocalization of electrons with the benzene ring. The most probable explanation to this phenomena may be that the nitrogen compounds are not permanent catalyst poisons but their effect on reaction rate is completely reversible and species such as pyrroles, are involved which participate in reactions leading to catalyst poisoning.

Several other investigators<sup>1,2,4</sup> have also suggested that there is a minimum concentration of basic nitrogen which has an immediate effect on the active sites of HDS. From Fig. 1 it may also be observed that for the feed of constant sulfur content of 0.78%, the HDS activity of Ni Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is unaltered for nitrogen concentrations upto 0.2% whereas the

nitrogen has a stronger inhibiting effects at higher nitrogen concentrations.

*Effect of H<sub>2</sub>S on HDN*—Fig. 2 shows the effect of H<sub>2</sub>S partial pressure on per cent denitrogenation at 390°C, 2.75 MPa and 30 minutes reaction time. It may be observed that as the nitrogen concentration in the feed is increased (from 0 to 1 wt % nitrogen), the H<sub>2</sub>S partial pressure in the reactor atmosphere would decrease owing to the inhibition of HDS. If the variation in the extent of nitrogen in the feed is considered not much in comparison to the variation in the H<sub>2</sub>S partial pressure in the reactor atmosphere, it may be concluded that there is a pronounced effect of H<sub>2</sub>S on HDN. The HDN rate is seen to increase as the H<sub>2</sub>S partial pressure has increased from 12.1 kPa to 33.5 kPa whereas with further increase in H<sub>2</sub>S partial pressure from 33.5 to 53.7 kPa the HDN rate decreased. A similar phenomena was observed by the earlier investigators<sup>1</sup>, where the HDN rate increased with the increase in H<sub>2</sub>S partial pressure from 0 to 13.3 kPa, but on the contrary to our observations, the percent HDN was substantially unaffected by the presence of H<sub>2</sub>S at its partial pressures from 13.3 to 26.6 kPa. The reasons for this deviation may be attributed to the decreasing concentration of the nitrogen in the feed in our case, which may have directly affected the rate of HDN. The effect of H<sub>2</sub>S on

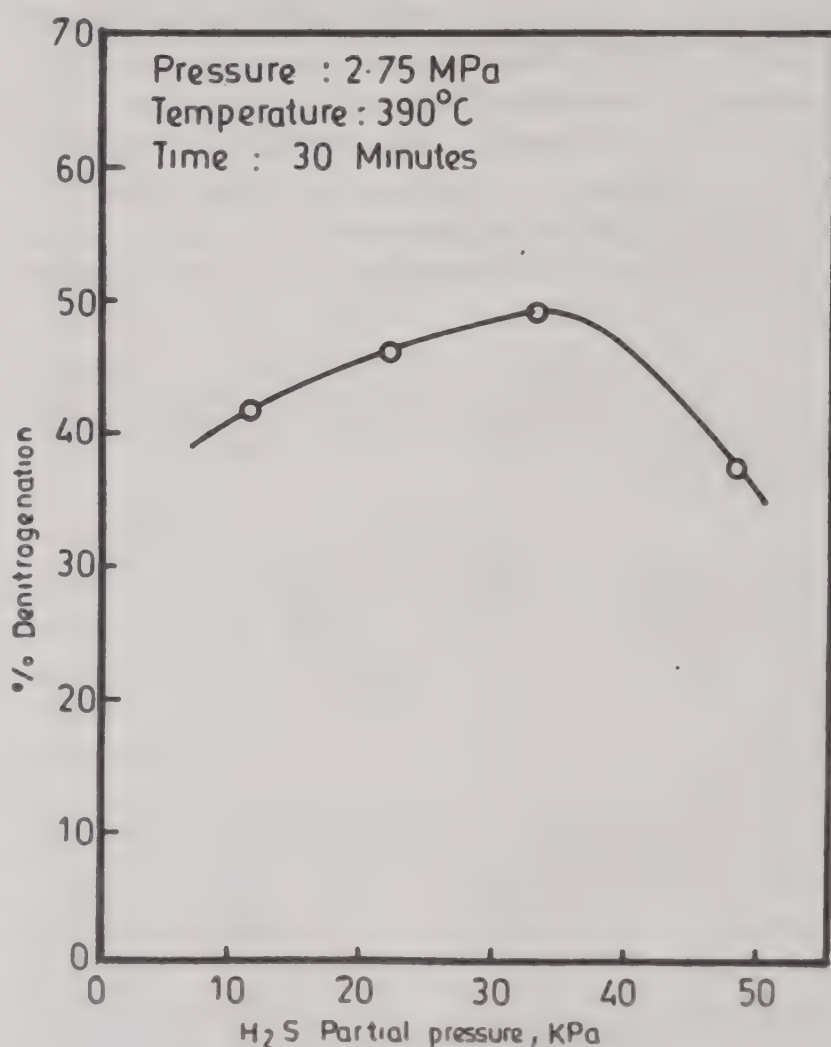


Fig. 2—Effect of H<sub>2</sub>S on % hydrodenitrogenation



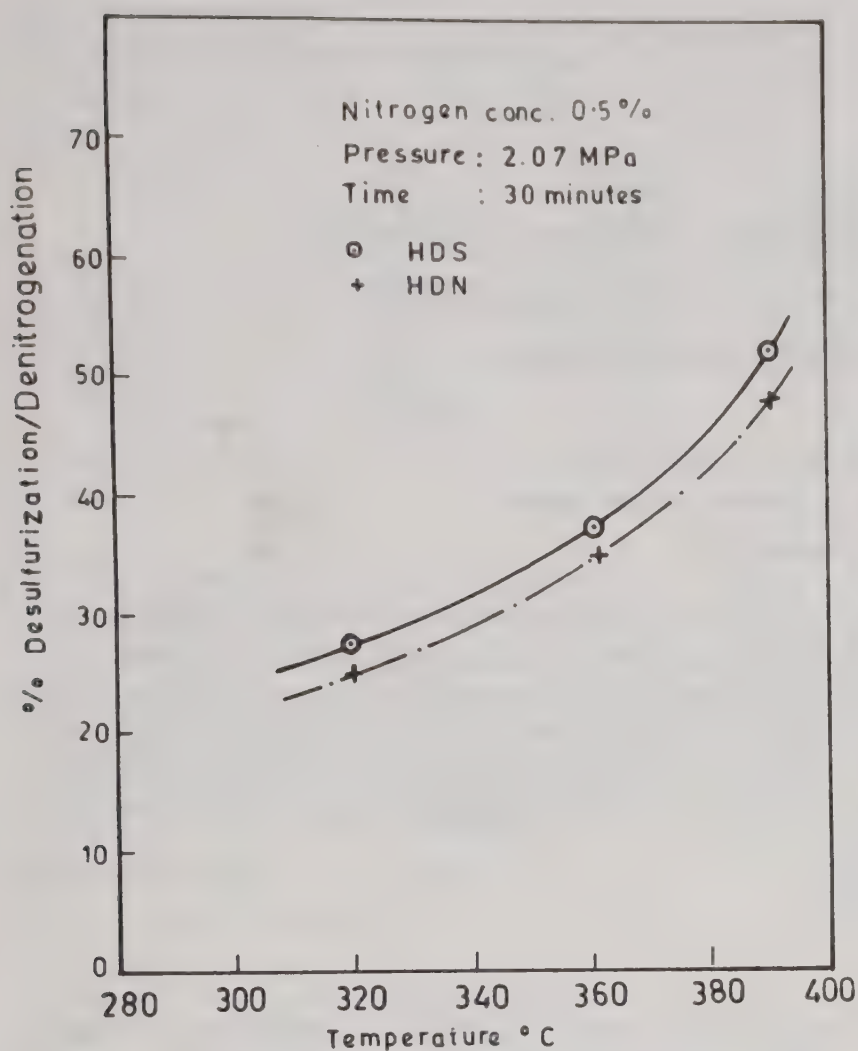


Fig. 3—Effect of temperature on % HDS/HDN

increasing HDN upto a certain partial pressure of  $H_2S$  may be explained on the basis that the presence of  $H_2S$  maintains the catalyst in a completely sulfided state which has better nitrogenation activity.

Experiments showed that due to the exposure of hydrogen at reaction temperature for sufficiently long time the sulfur content was reduced considerably below the amount of sulfur required for a completely sulfided catalyst.

Denitrogenation in comparison to desulfurization has always been found to be more difficult. Figure 3 shows the effect of temperature on both HDS and HDN at identical operating conditions.

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## Effect of atomic (O/C) ratio and helium density on microwave desulphurization efficiencies and correlations for their predictions

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In microwave desulphurization atomic O/C ratio and helium density of coal are found to be very important parameters. The sulphatic sulphur removal efficiency is found to correlate linearly with atomic O/C ratio. The pyritic sulphur removal efficiency is found to correlate with atomic O/C ratio and helium density with correlation coefficients of 0.998 and 0.995 respectively. The organic sulphur removal efficiency is found to correlate with atomic O/C ratio and helium density with correlation coefficients of 0.999 and 0.97 respectively. The total sulphur is also correlated with atomic O/C ratio with high degree of correlation coefficients.

The environmental pollution and strict regulations have become serious problem with the increased use of high sulphur coals in wide variety of industrial applications. Today, large member of desulphurization processes based on biological, physical and chemical methods are available. Among the various developed processes the microwave<sup>1-4</sup> desulphurization has good potential with high thermal efficiency. In microwave desulphurization reaction, the temperature of coal rises to the modest level of between 50°C to 150°C with no significant evolution of hydrogen or carbon containing matter. In this process only 0.3 to 1.0 per cent of the heating value of coal is necessary to volatilize the sulphur in the form of stable gaseous compound. It has also been indicated that the process of microwave desulphurization<sup>4</sup> is closely related to the chemical and physical structure of coal. Molecular structure of coals on the other hand may be adequately related to atomic O/C ratio<sup>5,6</sup> and helium density<sup>7</sup>. In relation to oxidation studies of high sulphur coal Singh<sup>8</sup> has shown the correlation of higher order between oxidation time and atomic O/C ratio. In another work Singh<sup>9</sup> has established linear relationships between carboxyl acidity and atomic O/C ratio with a correlation coefficient of very high order. Recently, Singh and Kakati<sup>10</sup> have also obtained a correlation between specific energy and atomic O/C ratio.

In view of its importance and potentiality, an attempt has been made in present study to examine the effect of some important coal parameters, such as

atomic O/C ratio and helium density on sulphatic sulphur, pyritic sulphur, organic sulphur removal efficiencies and also to establish correlations between them for their prediction.

### Data and Methods

Data for the investigation and establishment of various correlations are derived from Yang and Wu<sup>4</sup> works. For evaluating constants some data points were interpolated (3 nos.) using Spline technique of numerical analysis. Helium density of coals was calculated from correlations proposed by Mazumdar<sup>7</sup>. Data on atomic O/C ratio and helium density of various coals and microwave desulphurization efficiency (using sodium hydroxide as a leachant and single exposure of 60 seconds with a microwave source of 2-3 KW and 2450 MHz) pertaining to various forms of sulphur are presented in Table 1.

### Results and Discussion

The combination of short wave length and high frequency enables microwaves to heat the coal molecules more effectively than conventional heating methods. Coal molecules being polar, it absorbs microwaves energy more easily causing resonance and thus generating direct frictional heat. Microwave heating is also more effective because heating proceeds from inside to outside, unlike conventional heating system where heat flows from outside to inside.



Table 1—Microwave desulphurization data with respect to atomic O/C ratio and helium density of various coals

Sample	Parameters		Wt per cent desulphurization efficiency <sup>a</sup>			
	Atomic (O/C) ratio	Helium density	Sulphatic sulphur	Pyritic sulphur	Organic sulphur	Total sulphur
Z-coal	0.0332	1.2191	95	97	66	76
W-coal	0.0516	1.2499	95	94	74	78
S-coal	0.0892	1.2656	97	93	60	70.6
X-coal	0.1319	1.3172	98	95	35	75.1

### Relation between atomic O/C ratio and sulphur removal efficiencies

Figure 1a presents the relationship between atomic O/C ratio and sulphatic sulphur removal efficiency ( $Y_{oc}^S$ ) which is found to be linear with correlation coefficient ( $r$ ) of 0.974 and absolute average % error (AAPE) of 0.29. The relation between related parameters may be expressed as :

$$Y_{oc}^S = 93.40 + 36.68 (O/C) \quad \dots (1)$$

Relationship between O/C ratio and pyritic sulphur removal efficiency is shown in Fig. 1b, which is characterised by single minima. The regression equation with  $r = 0.999$  and AAPE = 0.04, may be expressed as :

$$Y_{oc}^P = 108.77 - 501.76 (O/C) + 4936.59 (O/C)^2 + 14590.80 (O/C)^3 \quad \dots (2)$$

Figure 2a presents the relationship between O/C ratio and organic sulphur removal efficiency. It is seen from the plot that increase of ratio causes to increase organic sulphur removal efficiency upto certain value only beyond which it decreases rapidly. This indicates that in microwave desulphurization, high value of O/C ratio may result in reduction of organic sulphur removal efficiency. The regression equation with  $r = 0.999$  and AAPE = 0.64 may be expressed as:

$$Y_{oc}^O = 12.29 + 2569.98 (O/C) - 32211.61 (O/C)^2 + 106462.87 (O/C)^3 \quad \dots (3)$$

The high values of correlation coefficients show that sulphatic sulphur, pyritic sulphur and organic sulphur removal efficiencies are highly interrelated with O/C ratio. The fitting of polynomials (1), (2) and (3) are shown in Fig. 3. The relationship between O/C ratio and total sulphur removal efficiency is shown in Fig. 2b. Total sulphur removal efficiency is the summation of various forms of sulphur removal efficiencies. Therefore, increase or decrease of total sulphur removal efficiency is the overall cumulative effect of sulphatic, pyritic and organic sulphur removal efficiencies. Organic sulphur removal efficiency is found to be dominating factor for coals

having low range of O/C ratio. For coals having values between 0.05 to 0.09, both pyritic and organic sulphur removal efficiencies are observed to decrease and therefore, total sulphur removal efficiencies are found to be dominating factor. The relationship

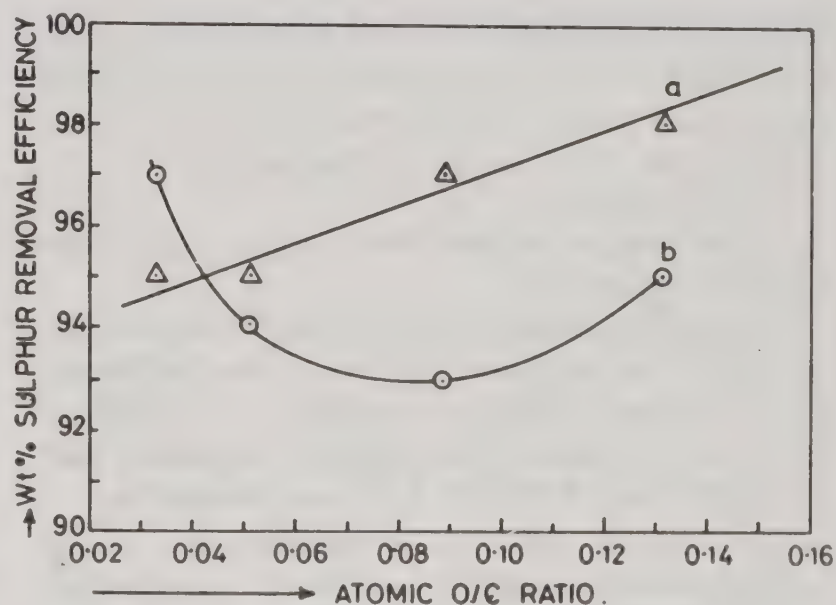


Fig. 1—Relation between atomic (O/C) ratio and sulphur removal efficiency :  $\Delta$  sulphatic;  $\circ$  pyritic

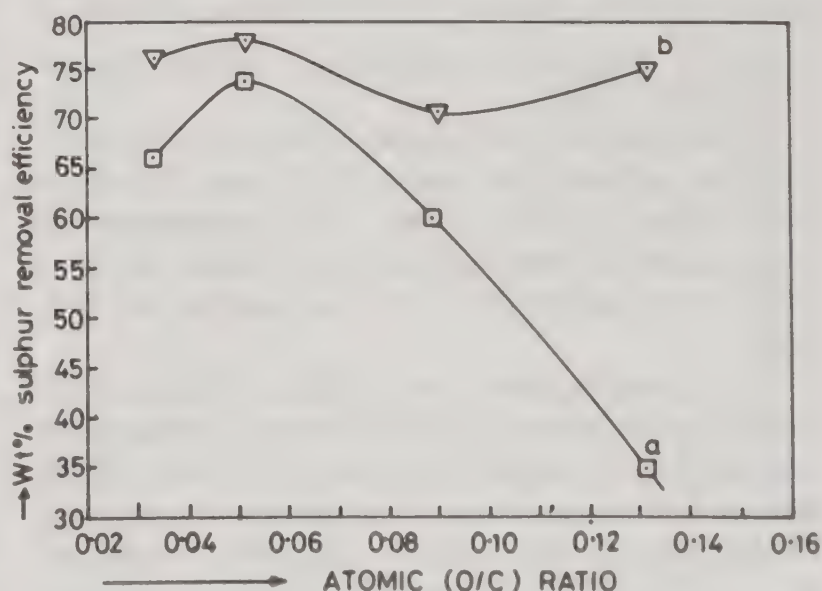


Fig. 2—Relation between atomic (O/C) ratio and sulphur removal efficiency :  $\square$  organic;  $\triangleright$  total



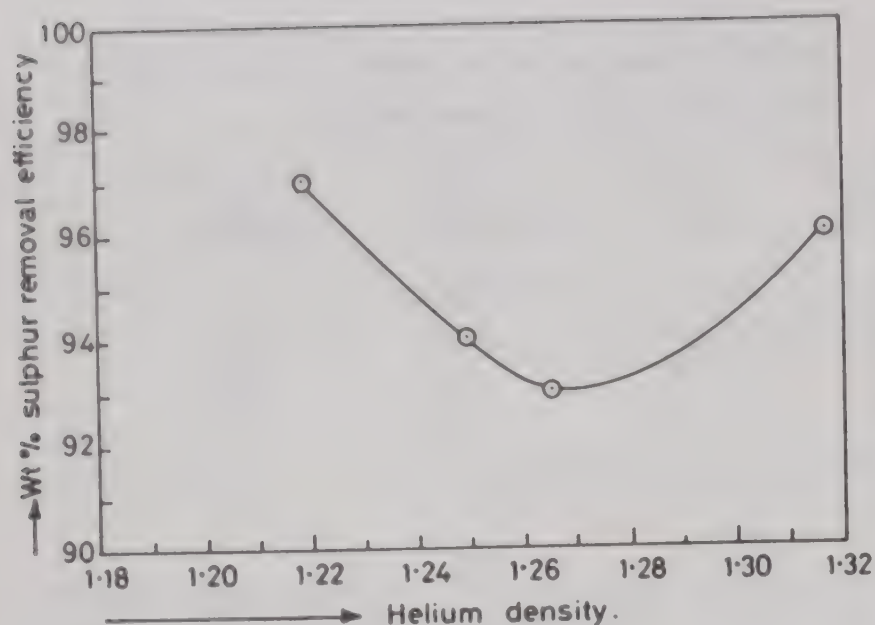


Fig. 3—Relation between experimental and predicted value of sulphur removal efficiency :  $\Delta$  sulphatic  $\odot$  pyritic;  $\square$  organic

between total sulphur removal efficiency ( $Y_{oc}^T$ ) and O/C ratio can be expressed by the following polynomial with  $r = 0.982$  and  $AAPE = 0.57$ .

$$Y_{oc}^T = 54.64 + 1143.77 (O/C) - 17391.58 (O/C)^2 + 75131.30 (O/C)^3 \quad \dots (4)$$

Relation between helium density ( $d_{He}$ ) and sulphur removal efficiencies

Figure 4 presents the relationship between helium density of coal and pyritic sulphur removal efficiency ( $Y_{He}^P$ ), where minimum frequency is exhibited towards the centre. The regression equation with  $r = 0.997$  and  $AAPE = 0.12$  is expressed as :

$$Y_{He}^P = 2112.48 - 3162.38 d_{He} + 1238.00 (d_{He})^2 \quad \dots (5)$$

High value of correlation coefficient indicates that pyritic sulphur removal efficiency is highly interrelated with helium density.

The relationship with  $r = 0.997$  and  $AAPE = 1.36$  between organic sulphur removal efficiency ( $Y_{He}^O$ ) and helium density ( $d_{He}$ ) can be represented as :

$$Y_{He}^O = -505147.56 + 1192148.25 d_{He} - 936998.19 (d_{He})^2 + 245296.56 (d_{He})^3 \quad \dots (6)$$

Weathering of coals causes to increase both the sulphatic sulphur and atomic O/C ratio. The close association between these two parameters are responsible for strong linear relationship between sulphatic sulphur removal efficiency and atomic O/C ratio.

The organic sulphur is bounded directly to the coal matrix and its removal probably depends on degree of destruction of organic structure of coal. Pyritic sulphur and oxygen containing functional groups are interlinked with coal structure. Atomic O/C ratio and helium density are also closely related to coal structure. Because of these close inter relationship between related parameters, organic and pyritic

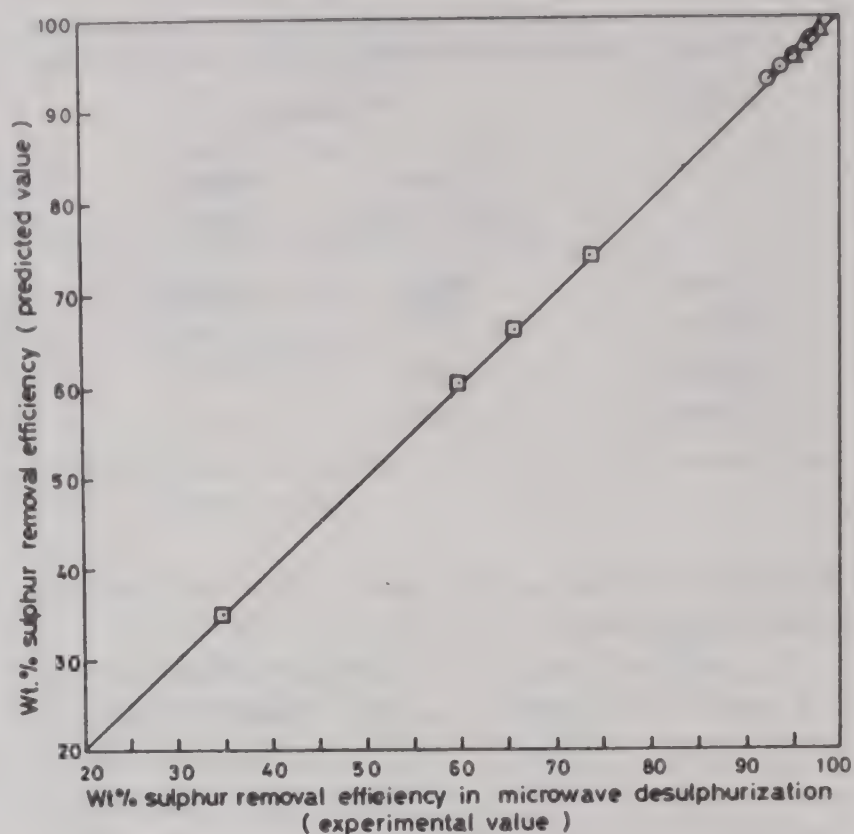


Fig. 4—Relation between helium density and wt % sulphur removal efficiency :  $\odot$ ; pyritic

sulphur efficiencies resulted strong correlations with O/C ratio and helium density.

## Conclusion

Microwave desulphurization has good potentiality with high thermal efficiency for reducing various forms of sulphur from coals in a very effective way. Linear relationship is found to exist between sulphatic sulphur removal efficiency and atomic O/C ratio with high degree of correlation coefficient. Increase in O/C ratio is found to decrease the pyritic sulphur removal efficiency up to certain fixed value only, beyond which its increase is found to be beneficial. The strong relationship is found to exist between pyritic sulphur removal efficiency and atomic O/C ratio of coal. Similar relationship is found to exhibit between pyritic sulphur removal efficiency and helium density with high degree of correlation coefficient.

Increase in O/C value of coal is found to be helpful in removing organic sulphur up to certain fixed value only, beyond which its increase is not beneficial. Organic sulphur removal efficiency correlates with the atomic O/C ratio and helium density strongly. The strong relationship is also found to exist between total sulphur removal efficiency and atomic O/C ratio of coal. The developed models will be of immense utility in predicting microwave desulphurization efficiencies at given conditions by knowing elemental compositions of coals under interest.



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**NOMENCLATURE**


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O/C	Atomic oxygen to carbon ratio.
$Y_{oc}^S$	Predicted value of sulphatic sulphur removal efficiency based on atomic O/C ratio.
$Y_{oc}^O$	Predicted value of organic sulphur removal efficiency based on atomic O/C ratio.
$Y_{He}^O$	Predicted value of organic sulphur removal efficiency based on helium density.
$Y_{oc}^P$	Predicted value of pyritic sulphur removal efficiency based on atomic O/C ratio.
$Y_{He}^P$	Predicted value of pyritic sulphur removal efficiency based on helium density.
$Y_{oc}^T$	Predicted value of total sulphur removal efficiency based on atomic O/C ratio.
$x_1$	Atomic O/C ratio
$x_2$	Helium density.
$r$	Correlation coefficient.
AAPE	Absolute average % error

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## Studies on alkoxygen and alkoxygen – anthroquinone delignification of *Ipomea carnea*

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The proposed study was undertaken to assess the suitability of *Ipomea carnea* by alkoxygen delignification process and to know the effect of anthraquinone (AQ) on pulp and paper characteristics. The comparatively loose and more open structure and low specific gravity of *I. carnea* chips, make it possible to diffuse dissolved oxygen easier to accomplish alkoxygen and alkoxygen-AQ delignification of *I. carnea*. The effect of cooking variables like oxygen pressures (0, 5, 8, 10 and 12 kg/cm<sup>2</sup>), alkali charge (14, 16 and 18%, as Na<sub>2</sub>O), cooking time (60, 90, 120 and 150 min), cooking temperatures (150, 155, 160 and 165°C) and AQ dose (0, 0.05, 0.1 and 0.2%, on o.d. wood basis), on pulp yield, kappa number, screening rejects and strength properties were evaluated. The alkoxygen-AQ delignification of *I. carnea* led to a significant increase in screened pulp yield, faster rate of delignification alongwith substantial drop in kappa number, due to stabilisation of carbohydrates towards end wise degradation. The results of these studies revealed that the following process conditions could be considered as optimum values for alkoxygen and alkoxygen-AQ pulping of *I. carnea* (alkali dose-16% as Na<sub>2</sub>O, temperature-160°C, time at temperature-120 minutes, oxygen pressure-10 kg. cm<sup>2</sup> and AQ dose 0.1%). These pulps beat fast and the optimum degree of beating was found to be around (42 ± 2°SR), in order to preserve tear and opacity. The unbleached pulps showed good response for bleaching by CEH and/or CEHH bleaching sequence to attain a brightness level of around 76% (Elrepho). Both unbleached and bleached pulps showed good level of strength properties to be used for making various grades of paper. The total solid content of *I. carnea* spent liquor was high, thereby increasing the calorific value. The silica content was found to be quite low. The alkoxygen-AQ pulping gave positive and very promising results for the possibilities of improving the existing soda pulping method to one that is fully commensurate with kraft process, with comparatively low pollution load. It can also be concluded that AQ has a favourable influence not only on increasing pulp yield with improved strength properties, but also reduce the pollution load to preserve the natural eco-balance of the environment.

It is well known that oxygen in an alkaline medium can be used as a delignifying agent in pulp bleaching both as a substitute for chlorine, as well as a true delignifying agent for chemical pulping. Although it is accepted that molecular oxygen is a specific oxidising agent for lignin, an immediate draw-back to its use is the low solubility in cooking liquors. This causes a serious problems of mass transfer in a heterogeneous chemical process such as wood pulping. Even applying very high dose of oxygen, useful mass transfer of the delignifying agent (molecular oxygen) into the fiber walls, where the reaction should take place, is difficult to obtain in one stage pulping<sup>1</sup>. Many efforts have been made in the development of two stage alkali-oxygen delignification of wood to give pulps comparable to kraft, in yield and quality<sup>2-4</sup>. These generally involve a mild cooking stage followed by mechanical defibration. The coarse pulp thus obtained is very suitable for

subsequent alkaline treatment in the presence of oxygen due to its higher exposed surface<sup>5-9</sup>; but unfortunately the two stage pulping process is rather cumbersome and likely to be high in capital costs. Afterwards, instead of wood chips, thermomechanical fibers have been used for alkali-oxygen pulping<sup>5-9</sup> to develop one stage oxygen pulping, but some strength deficiencies have taken place, originating from mechanical damage caused in the pressurised refining, which itself is an operation, high in energy consumption<sup>10</sup>.

Environmental control laws on industrial emission, particularly the emission of sulphur compounds together with the need of more effective utilisation of raw materials have contributed to the intensive work done in recent years for the development of cooking methods which will give similar pulp qualities and preferably higher yields than the kraft process, without the addition of sulphur compounds. One such method might be the old soda process, if only the yield and pulp quality could be improved.

\* For correspondence



Many different additives have been used to improve the yield and quality of soda pulp. Among the additives anthraquinone (AQ) was found to produce quite encouraging results. It appears that AQ is still the most cost-effective sulphur-free accelerator for alkaline pulping, albeit of limited applications. The soda-AQ process does offer a direct advantage of eliminating air pollution associated with kraft process.

Unlike that of wood, in *I. carnea* the problems of mass transfer of delignifying agent (Molecular oxygen) should be much less important, since the plant structure should permit much easier diffusion and penetration of the delignifying agent into the reactive zones of fiber wall. The loose and open structure and low lignin content of *I. carnea* makes it suitable to perform soda-oxygen and soda-oxygen-AQ pulping.

### Experimental Method

**Raw material and its preparation**—The stalks of *I. carnea* were collected from nearby regions of Saharanpur, and were chopped by hand and screened. The chips those passing through 30 mm screen but retained on a 20 mm screen were collected. The accepted chips were air dried under atmospheric conditions.

The selected air dry material was disintegrated in the laboratory WEVERK disintegrator. The portion of wood meal passing through 40 mesh sieve but retained on 80 mesh sieve was utilized for proximate chemical analysis. The proximate chemical analysis was carried out as per TAPPI standard procedures. The chemical composition of *I. carnea* is reported in Table 1.

**Pulping studies**—Screened *I. carnea* chips were cooked in electrically heated rotary digester of 0.02 M<sup>3</sup> capacity having 4 bombs of one liter capacity, furnishing sufficient pulp for evaluation as well as for conducting bleaching experiments. To determine the optimum pulping condition during the course of pulping, a number of experiments were conducted at different conditions by varying the different process variables such as alkali charge (14, 16 and 18%, as Na<sub>2</sub>O), oxygen pressure (0, 5, 8, 10 and 12 kg/cm<sup>2</sup>), temperature (150, 155, 160 and 165°C) and AQ doses (0.0, 0.05, 0.1 and 0.2% on o.d. wood basis). During the course of pulping the liquor to wood ratio of 3.5:1 was used with following time schedule for heating the digester.

Time from room temperature to 105°C = 45 minutes.

Time from 105°C to maximum temperature = 45 minutes.

Table 1—Proximate chemical analysis of *I. carnea*

Sl. No.	Particulars	Percentage
1	Cold water solubles, (%)	3.90
2	Hot water solubles, (%)	9.30
3	Alcohol benzene solubles, (%) (1:2V/V)	4.65
4	1% Sod. hydroxide solubles, (%)	24.44
5	Lignin, (%)	16.59
6	Pentosan, (%)	17.30
7	Hemicellulose, (%)	21.20
8	Holo cellulose, (%)	72.00
9	Alpha cellulose, (%)	43.21
10	Beta cellulose, (%)	10.00
11	Gamma cellulose, (%)	18.00
12	Ash, (%)	6.45
13	Silica, (%)	0.16
14	Acetyl content, (%)	2.05
15	Methoxyl content, (%)	3.06

During cooking, the digester pressure was reduced by gas relief until the temperature reached to 105°C. the charge was then blown from the digester and the chips were defibred through a Bauer refiner with a plate clearance of 0.15 mm followed by second pass at 0.07 mm plate clearance. The pulp was screened through a laboratory vibratory flat WEVERK screen with 0.15 mm slits and the screened pulp was washed, pressed and crumbled. The yield, rejects and Kappa number were determined. The spent liquor was analysed for total solids, inorganics, organics, silica, BOD and COD. All the results of pulping as well as spent liquor analysis are reported in Table 2 to 9.

**Bleaching studies**—The *I. carnea* pulp showed good response towards bleaching and were bleached with conventional CEHH bleaching sequence to get pulp of higher brightness. The bleaching conditions along with results are given in Table 6.

**Pulp evaluation**—The unbleached and bleached pulps were beaten in PFI mill with a beating pressure of 1.8 kg/cm to different freeness levels and hand sheets of 60 gm/cm<sup>2</sup> were prepared on standard British sheet forming machine. These hand sheets were evaluated as per BIS method for their different physical strength properties at a temperature of 27 ± 2°C and at a relative humidity level of 65 ± 2%. The pulp evaluation results are recorded in Table 5, 7 and 8.

**Fibre classification studies**—The fibre classification studies of *I. carnea* pulps were made with the help of Bauer-McNett fibre classifier using screens



Table 2—Effect of oxygen pressure and alkali charge on pulp yield of *I. carnea*

Fixed cooking parameters :  
 Time from room temp. to 105°C = 45 minutes  
 Time from 105°C to 160°C = 45 minutes  
 Time at 160°C = 120 minutes  
 Liquor to wood ratio = 3.5:1

Alkali dose, % (as Na <sub>2</sub> O)	Oxygen pressure, (kg/cm <sup>2</sup> )	Pulp yield, (%)	Screening rejects, (%)	Screened yield, (%)	Kappa No.,	Spent liquor pH
14	0	50.67	4.10	46.57	49	8.7
	5	51.90	2.90	49.00	43	8.6
	8	52.40	2.40	50.20	40	8.1
	10	52.45	2.20	50.25	38	8.0
	12	49.55	2.05	47.50	37	7.9
16	0	48.53	3.25	45.28	39	10.3
	5	50.20	1.70	48.50	33	9.2
	8	50.25	1.25	49.00	30	9.3
	10	49.85	0.75	49.10	29	9.4
	12	46.00	0.50	45.50	28	9.4
18	0	44.20	2.60	41.60	32	10.5
	5	44.75	1.25	43.50	25	9.4
	8	44.85	0.85	44.00	22	9.6
	10	45.50	0.50	45.00	20	9.6
	12	42.80	0.30	42.50	19	9.2

Table 3—Effect of temp. during alkali-oxygen delignification of *I. carnea*

Fixed cooking parameters :  
 Active alkali = 16% (as Na<sub>2</sub>O)  
 Oxygen pressure = 10 kg/cm<sup>2</sup>  
 Liquor to wood ratio = 3.5:1

Sl. No.	Temp., °C	Pulp yield, (%)	Screening rejects, (%)	Screened yield, (%)	Kappa No.,	Spent liquor pH
1	150	48.10	3.50	44.60	39	9.9
2	155	48.00	1.50	46.50	33	9.7
3	160	49.85	0.75	49.10	29	9.4
4	165	42.10	0.25	41.85	27	9.1

Table 4—Effect of time during alkali-oxygen delignification of *I. carnea*

Fixed cooking parameters :  
 Maximum temperature = 160°C  
 Oxygen pressure = 10 kg/cm<sup>2</sup>  
 Liquor to wood ratio = 3.5:1

Sl. No.	Time at max. temp., (min.)	Pulp yield, (%)	Screening rejects, (%)	Screened yield, (%)	Kappa No.,	Spent liquor pH
1	60	50.60	6.0	44.60	39	10.0
2	90	49.80	3.5	46.30	40	9.9
3	120	48.90	0.75	48.15	29	9.4
4	150	44.80	0.50	44.30	27	8.9

Table 5—Comparison of soda, soda-oxygen and soda-oxygen-AQ delignification of *I. carnea* at 16 per cent alkali dose, 160°C temperature and 2 hours time at temperature

Sl. No.	Oxygen pressure, (kg/cm <sup>2</sup> )	AQ dose, (%)	Pulp yield, (%)	Rejects (%)	Screened yield, (%)	Kappa No.,	Spent liquor, pH	Burst Index, (K.pa.m <sup>2</sup> /g)	Tensile Index, (Nm/g)	Tear Index, (m.N.m <sup>2</sup> /g)	Folding endurance, (no.)
1	0	0.0	48.50	3.25	45.28	39	10.3	3.61*	68.00*	4.05*	3*
2	5	0.0	48.70	1.70	47.00	36	9.2	3.60	67.00	4.05	150
3	5	0.1	48.90	1.50	47.40	32	9.2	3.63	67.50	4.05	170
4	8	0.1	48.95	1.15	47.70	29	8.9	3.65	68.00	4.10	175
5	10	0.05	49.00	0.50	48.50	28	8.8	3.66	68.00	4.16	190
6	10	0.1	49.10	0.30	48.80	27	8.8	3.68	70.00	4.17	200
7	10	0.2	48.10	0.10	48.00	26	8.8	3.67	69.00	4.15	210

\*Time at temperature 165°C = 3 hours; Freeness = 45°SR.

with mesh number 28, 60, 80 and 150. The results of fibre classification studies are reported in Table 10.

### Results and Discussions

The results of proximate chemical analysis showed that the plants of *I. carnea* have moderate quantities of solubles thereby creating lesser pitch troubles with improved homogenities in the paper sheet. These plants have low lignin and comparatively higher total carbohydrate fraction (in comparison to other non-woody materials), thereby require less amount of cooking chemicals with shorter cooking cycles.

The effect of following variables on pulp yield and degree of delignification were studied in order to get their optimum level.

Oxygen pressure  
 Alkali charge  
 Cooking temperature  
 Cooking time  
 Anthraquinone (AQ) dose

Table 2 shows the results of alkali delignification of *I. carnea* at different alkali charges 14, 16 and 18 per cent (as Na<sub>2</sub>O), with and without oxygen under



pressure 0, 5, 8, 10 and 12 kg/cm<sup>2</sup> at fixed cooking parameters, temperature 160°C, time to temperature 90 minutes, time at temperature 120 minutes and bath ratio 1:3.5. Fig. 1 shows that under otherwise cooking conditions, oxygen has a considerable effect on cooking parameters.

Table 6—Bleaching conditions and results of alkali-oxygen and alkali-oxygen-AQ pulps of *I. carnea*

Sl. No.	Particulars	Alkali-oxygen pulp	Alkali-oxygen-AQ-pulp		
1	Unbleached Kappa No.	29	27		
	Chlorination stage (C)				
	Amount of Cl <sub>2</sub> added on pulp (%)	5.50	5.00		
	Amount of Cl <sub>2</sub> consumed on pulp (%)	5.48	4.98		
	Amount of Cl <sub>2</sub> consumed on Cl <sub>2</sub> basis (%)	99.6	99.6		
	Final pH	2.05	2.05		
3	Alkali extraction stage				
	NaOH added on pulp (%)	2.78	2.53		
	Initial pH	11.59	11.61		
	Final pH	10.20	10.26		
4	Hypochlorite stage (H <sub>1</sub> )				
	Hypo added as available Cl <sub>2</sub> on pulp (%)	1.09	1.02		
	Hypo consumed as available Cl <sub>2</sub> on pulp (%)	1.05	1.00		
	Hypo consumed on Cl <sub>2</sub> basis (%)	96.3	98.03		
	Final pH	8.23	8.17		
5	Hypochlorite stage (H <sub>2</sub> )				
	Hypo added as avail Cl <sub>2</sub> on pulp (%)	0.73	0.68		
	Hypo consumed as avail Cl <sub>2</sub> on pulp (%)	0.70	0.67		
	Hypo consumed on pulp (%)	95.89	98.52		
	Final pH	8.17	8.20		
6	Total Cl <sub>2</sub> added on pulp (%)	7.25	6.75		
7	Total Cl <sub>2</sub> consumed on pulp (%)	7.23	6.75		
8	Bleaching losses (%)	10.01	10.10		
9	Bleached pulp yield	44.18	43.87		
10	Pulp brightness (Elrepho) %	76	76		
	Bleaching conditions :	C	E	H	H
	Consistency (%)	4	9	10	10
	Temperature (°C)	25±2	55±2	45±2	45±2
	Time (minute)	40	60	60	120

Pulping of *I. carnea* chips with soda-oxygen resulted in an increase in pulp yield from 5-9 per cent over that obtained from soda pulps prepared under the same pulping conditions. Increasing oxygen pressure from 0 to 10 kg/cm<sup>2</sup> increased the pulp yield attaining the maximum value and a further increase in oxygen pressure beyond 10 kg/cm<sup>2</sup> resulted in a slight decrease in pulp yield. The maximum carbohydrate yield was obtained at a oxygen pressure of 10 kg/cm<sup>2</sup>.

Table 2 indicates the results of alkali oxygen delignification of *I. carnea* at different doses of alkali with varying oxygen pressures. As far as the effect of delignification is concerned it can be observed that an increase in caustic soda charge from 14 to 18 per cent (as Na<sub>2</sub>O) has a very positive effect on delignification, the Kappa number dropped from 49 to 19 depending upon oxygen pressure. Alkali charge also has an

Table 9—Alkali-oxygen-AQ spent liquor characteristics of *I. carnea* at optimum condition

Sl. No.	Particulars	Percentage
1	Black liquor solids, (%)	25.96
2	Residual active alkali, (gpl)	3.74
3	Inorganics, as NaOH, (%)	28.42
4	Organics, (%)	71.58
5	Silica, (%)	2.10
6	pH of liquor at 30°C	9.40
7	BOD 5 days at 20°C (mg/ml)	20015
8	COD (mg/ml)	71700

Table 10—Bauer-McNett fibre classification of alkali-oxygen and alkali-oxygen-AQ (unbleached) pulp of *I. carnea*

Sl. No.	Mesh size	Alkali-oxygen pulp, %	Alkali-oxygen-AQ pulp, %
1	+ 20	19.5	20.0
2	- 20 + 60	48.2	47.6
3	- 60 + 80	13.5	13.0
4	- 80 + 150	7.0	6.7
5	- 150	11.80	12.70

Table 7—Strength properties of alkali-oxygen and alkali-oxygen AQ unbleached pulp of *I. carnea* at optimum condition

AQ dose (%)	Beating time, (minutes)	Freeness, (°SR)	Drainage time, (seconds)	Tensile Index, (Nm/g)	Burst Index, (K.pa.m <sup>2</sup> /g)	Tear Index (m.N.m <sup>2</sup> /g)	Folding endurance no.
0.0	0	13	4	22.74	0.74	2.74	6
	8	22	9	49.00	2.25	5.25	63
	30	40	16	68.10	3.30	4.40	170
	33	45	19	69.00	3.66	4.21	175
0.1	0	15	4	24.21	0.84	3.10	6
	8	25	9	56.21	2.64	5.79	95
	30	40	16	69.20	3.48	4.60	188
	33	45	19	70.02	3.68	4.37	200



Table 8—Strength properties of alkali-oxygen and alkali-oxygen-AQ bleached pulp of *I. carnea* at optimum condition

AQ dose (%)	Beating time, (minutes)	Freeness, (°SR)	Drainage time, (seconds)	Tensile Index, (Nm/g)	Burst Index, (K.pa.m <sup>2</sup> /g)	Tear Index, (m.N.m <sup>2</sup> /g)	Folding endurance, No.	Brightness (Elrepho) (%)
0.0	0	16	5	23.21	0.83	2.90	8	76
	8	25	11	48.21	2.23	5.17	60	72
	20	40	16	67.21	3.27	4.33	150	70
	25	45	19	68.20	3.62	4.19	170	70
0.1	0	18	5	25.19	1.10	3.25	12	76
	8	25	11	55.20	2.51	5.61	80	72
	20	40	16	67.00	3.32	4.39	175	72
	25	45	19	69.21	3.64	4.23	190	71

important influence on pulp yield. An increase in alkali charge resulted in substantial yield loss. The increased delignification alone does not seem completely responsible for these losses. The screened pulp yield obtained at an alkali charge of 16 per cent (as Na<sub>2</sub>O) and oxygen pressure of 10 kg/cm<sup>2</sup> (Fig. 1) seems to be most acceptable value based on Kappa number. The screening rejects and Kappa number both are having indirect proportional relationship with alkali doses and/or oxygen pressure i.e. screening rejects and Kappa number both decreased continuously as a result of an increase in either alkali dose or oxygen pressure.

Table 3 (and Fig. 2) represent the results of alkali-oxygen cooks carried out at four different temperatures 150, 155, 160 and 165°C, keeping all other variables constant. These results clearly indicate that an increase in cooking temperature notably improve delignification. As the temperature increased from 150 to 165°C, the Kappa number dropped from 39 to 27. The pulp yield and screening rejects both are having indirect proportional relationship with temperature i.e. as the temperature increased both the pulp yield and screening rejects showed a continuously decreasing trend (Fig. 2). The optimum results were obtained at a temperature of 160°C.

Table 4 (and Fig. 3) showed the results of the alkali-oxygen cooks aimed at evaluating the effect of cooking time. The cooks were made for 60, 90, 120 and 150 minutes, keeping all other parameters constant. These results indicated that rejects and Kappa number both are having indirect proportional relationship with time i.e. as the cooking time increased, both the rejects and Kappa number decreased continuously (Fig. 3). As regards to delignification, it is having a directly proportional relationship with time i.e. as the time of cook increased, the amount of lignin removal also increased. The screened pulp yield obtained with a

cooking time of 120 minutes seems to be most acceptable value based on Kappa number.

As *I. carnea* had proved to be very much suitable for alkali-oxygen delignification, it was deemed interesting to evaluate the effect of AQ on pulp yield, rejects, Kappa number and other properties. Different doses of AQ viz. 0.0, 0.05, 0.1 and 0.2 per cent (on o.d. wood basis) were applied to the cooks made at optimum cooking parameters (i.e. at an alkali charge of 16% (as Na<sub>2</sub>O), temperature 160°C, time to temperature 90 minutes, time at temperature 120 minutes and bath ratio 1:3.5). The results of addition of different doses of AQ during alkali-oxygen delignification are tabulated in Table 5.

These results indicated that, on increasing AQ, doses the screened pulp yield increased up to a certain level and beyond that it decreased, while the Kappa number and rejects both showed a continuously decreasing trend. Considering all parameters, an AQ dose of 0.1 per cent (on o.d. wood basis) was found to be optimum to get highest pulp yield with comparatively lower rejects and Kappa number.

The unbleached pulp brightness was found to be around 32 per cent (Elrepho). The unbleached pulps were bleached using CEHH bleaching sequence for obtaining high degree of brightness. The results of bleaching studies (Table 6) indicated that the pulps of *I. carnea* showed excellent bleaching response. During chlorination stage, 60-70 per cent chlorine of the total chlorine demand was used. The alkali requirement was about 1.53 per cent in the extraction stage. About 20 and 15 per cent chlorine of total chlorine demand in the form of calcium hypochlorite were applied in hypochlorite (H<sub>1</sub>) and (H<sub>2</sub>) stages which resulted a pulp with brightness level of 78 per cent (Elrepho).

The results of unbleached and bleached pulps (Table 7 and 8) indicated that initial freeness level and



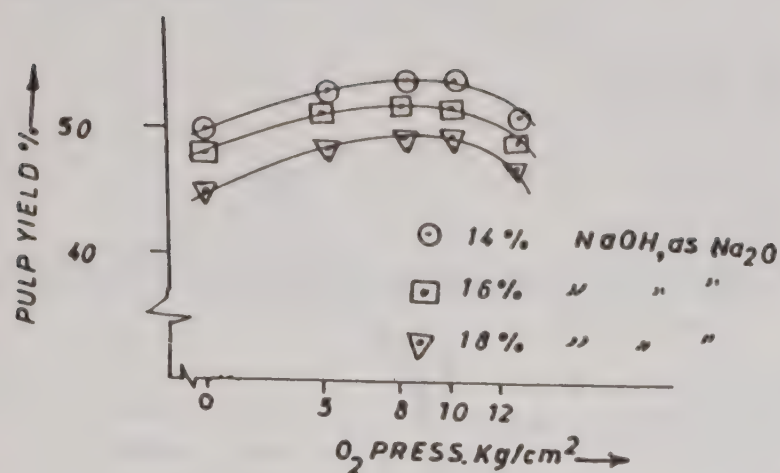


Fig. 1—Effect of oxygen pressure on pulp yield at different alkali dose

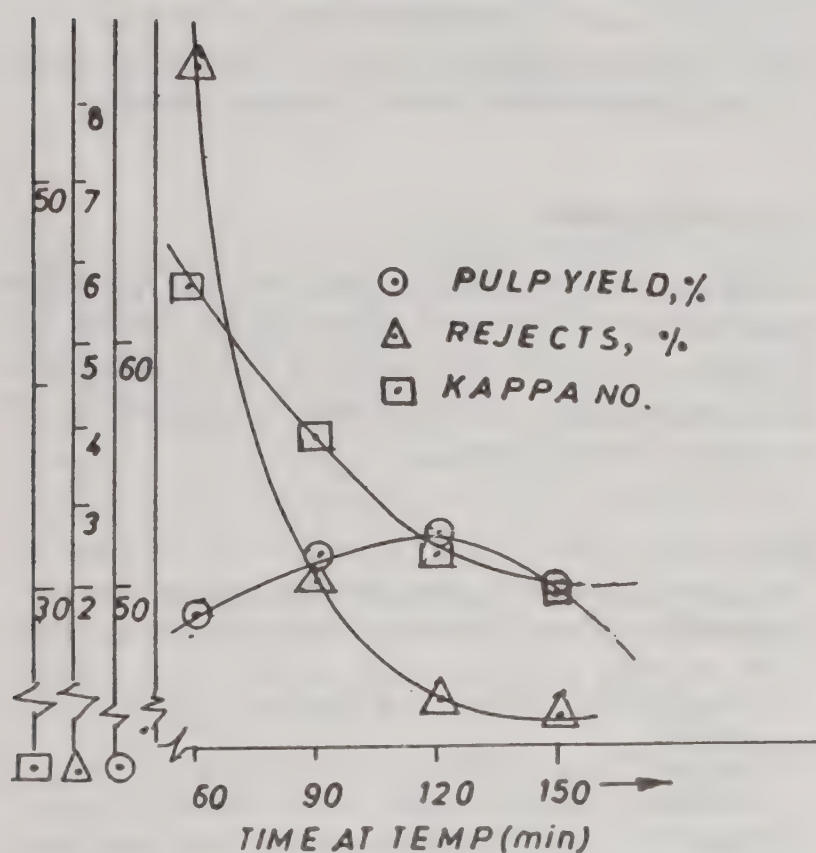


Fig. 3—Effect of time on pulp yield, Kappa No. and rejects

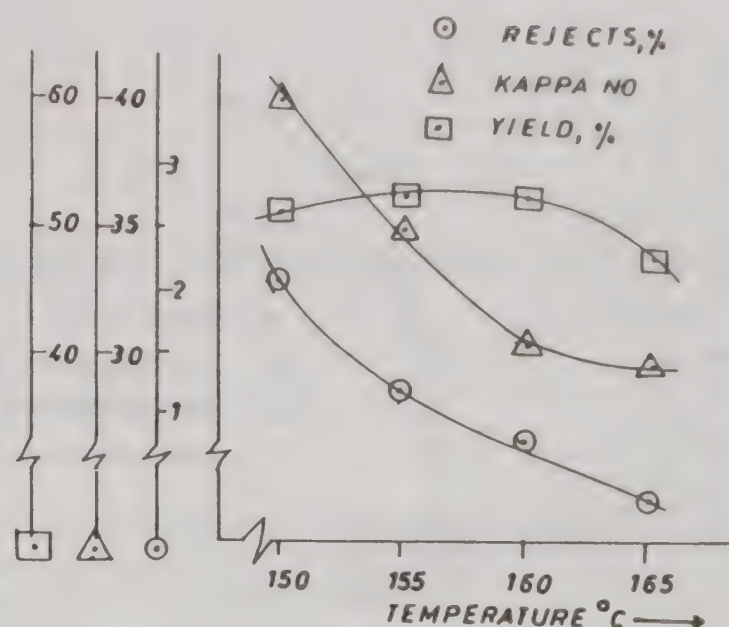


Fig. 2—Effect of temperature on pulp yield, Kappa No. and rejects

bleached pulps showed good strength characteristics. The optimum freeness level for these pulps may be considered around 40°SR. The physical properties of alkali-oxygen-AQ pulps showed over all improvement over alkali-oxygen pulps at same Kappa number.

The results of spent liquors analysis obtained from alkali-oxygen-AQ pulping under the optimum conditions (Table 9) indicated that the total solid contents were towards little higher side. The biochemical oxygen demand and chemical oxygen demand of spent liquor are slightly lower than the other non-wood fibres pulps. The silica content in the spent liquors were found to be very low. The lower silica and higher total solid contents are advantageous factor towards energy conservation in the chemical recovery system.

### Conclusion

The proposed study have ascertained that the soda-oxygen-AQ delignification of *I. carnea* is comparatively a better process. The lignin of these plants are much more sensitive to the action of oxygen and resulted a pulp with higher delignification. The delignification is easier than wood chips due to more open structure of *I. carnea* chips. There is no diffusion problem of dissolved oxygen into these non-wood plants because of its more loose structure and low specific gravity. Addition of AQ led to a significant increase in screened yield and rate of delignification compared to a soda, soda-oxygen pulping due to stabilisation of carbohydrates towards end-wise degradation. Addition of AQ may be economically beneficial due to substantial decrease in Kappa number, increase in pulp yield and strength

drainage rate was found to be quite higher. The freeness of unbeaten and beaten pulps were found to be around 13°SR respectively. The plots of pulp freeness (unbleached and bleached) versus burst, tensile, tear and folding endurance have shown in Figure 4 & 5 respectively. These plots indicated that burst index, tensile index and folding endurance are in directly proportional with the freeness of pulps i.e. all these strength properties showed an improving trend as a result of an increase in freeness level up to a certain level (i.e. around a freeness level of  $42 \pm 2^\circ\text{SR}$ ) and beyond that they showed a little decreasing trend, while the tear index for the unbleached and bleached pulps both, first showed a little enhancement (up to freeness level of about  $27 \pm 3^\circ\text{SR}$ ) and then showed a continuous decline trend. On the basis of these results, it can be concluded that both unbleached and



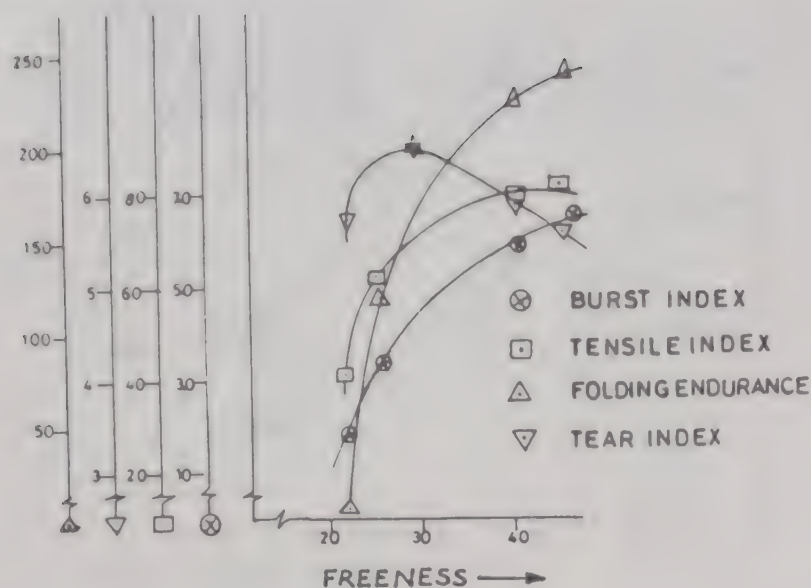


Fig. 4—Plots of strength properties vs freeness of alkali-oxygen-AQ unbleached pulps at optimum conditions

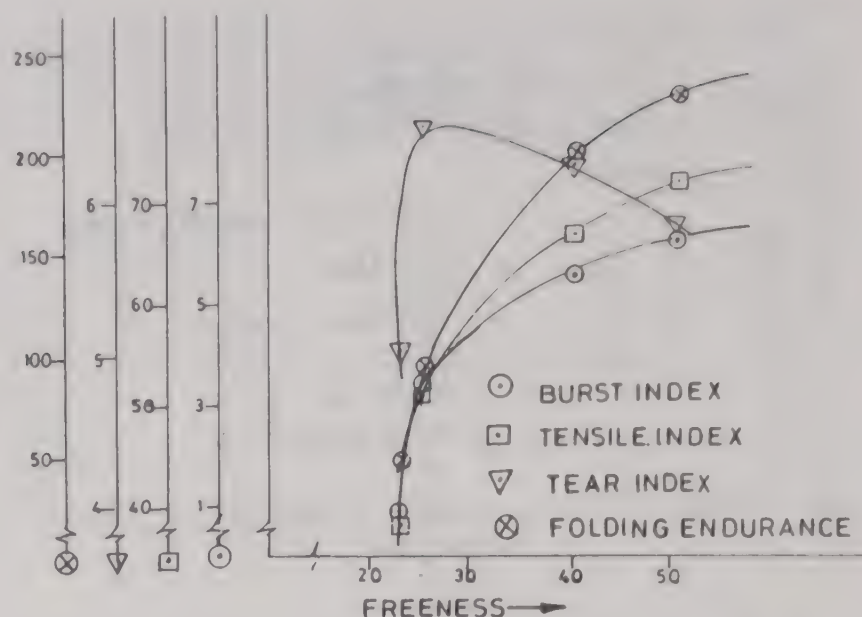


Fig. 5—Plots of strength properties vs freeness of alkali-oxygen-AQ bleached pulps at optimum condition

properties, and shorter cooking time. As regards the cooking variables it was found as follows.

The alkali charge is important for both delignification and yield. Better results were obtained at an alkali charge of 16 per cent (as  $\text{Na}_2\text{O}$ ).

An increase in cooking temperature bring about faster delignification. An optimum value of cooking temperature was observed at  $160^\circ\text{C}$ .

The cooking time of 120 minutes was found to be optimum for getting better delignification effects.

The AQ may be economically beneficial due to substantial decrease in Kappa number, increase in pulp yield and strength properties and shorter cooking time.

Based on our experimental results it can be concluded that optimum set of parameters for alkali-oxygen-AQ delignification of *I. carnea* may be consider as follows:

Alkali dose	16% as ( $\text{Na}_2\text{O}$ )
Oxygen pressure	10 $\text{kg}/\text{cm}^2$
Temperature	$160^\circ\text{C}$
Time at maximum temp.	120 minutes
Bath ratio	1:3.5
AQ dose	0.1%

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## Deoiling of hard microcrystalline wax by solvent percolation technique

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The study deals with the application of solvent percolation technique to separate oil from commercial microcrystalline wax flakes produced from Ankleshwar tank bottom sludges. Wax deoiling has been accomplished by percolating industrial hexane through a packed bed of the wax flakes at ambient temperature and removing the solvent from the wax and oil phases to get hard wax and foots oil respectively. The resultant product wax has oil content of about 2 per cent and needle penetration value of 4 at 25°C.

Commercially available indigenous microcrystalline wax, produced from Ankleshwar crude tank bottom sludges by Oil & Natural Gas Commission (ONGC), contains 9-12 per cent light lubricating oil. Microcrystalline wax with such a high oil content is unsatisfactory for many applications like paper coating, electrical insulation, textile printing and polishes. The deoiling processes<sup>1-3</sup> employed to upgrade the quality of such waxes involve extractive crystallization with ketones in scraped surface equipment and filtration in rotary-drum filters, thus rendering the process uneconomical for small scale industrial units.

Tank bottom microcrystalline wax has been found to be amenable to deoiling by solvent leaching using non polar organic solvent. Based on this observation, a deoiling process was developed for the production of low oil-content waxes by solvent leaching and settling filtration and the results have been reported in an earlier communication<sup>4</sup>. Main drawback of the leaching process lies in shearing of crude wax flakes yielding appreciable quantity of an intermediate mixed wax phase<sup>4</sup>. In the present study, mechanical mixing and filtration operations have been substituted to percolation of solvent through wax flakes, thereby eliminating mixed wax phase in the process. The results of the investigation carried out on this aspect are reported in the present communication.

### Materials and Method

#### Materials

Commercial microcrystalline wax in the form of fine flakes, as available from ONGC having melting point of 90.2°C and oil content of 11.2 per cent, was taken as feed stock (Table 1). Industrial hexane (b.p. 63-70°C) was used as solvent.

Table 1—Characteristics of the feed stock

Oil content, wt % (ASTM D-721)	11.2
Melting point, °C (ASTM D-127)	90.2
Kin. viscosity at 98.9°C, cSt (ASTM D-445)	11.0
Needle penetration, d mm (ASTM D-1321)	
at 25°C	12
at 35°C	20
Flash point, °C (ASTM D-92)	220
Colour (ASTM D-1500)	2
Distillation (ASTM D-1160)	
IBP, °C	280
5% vol. recovered at °C	325
10% vol. recovered at °C	355
20% vol. recovered at °C	410
30% vol. recovered at °C	475
35% vol. recovered at °C	500

#### Method

The wax flakes weighing around 800 g were randomly packed in a glass column (dia. 7 cm, length 120 cm). Hexane solvent was percolated under gravity over the packed bed of wax flakes from the top maintaining the temperature of the column at  $28 \pm 2^\circ\text{C}$ . Solvent percolation was stopped when the effluent was almost free from oil. Refractive Index and colour of the stream flowing out of the column were used for the process control. After the percolation run, wax and oil solution phases were made free from the solvent by distillation to get hard wax and foots oil respectively. The products were analysed following ASTM test procedures.



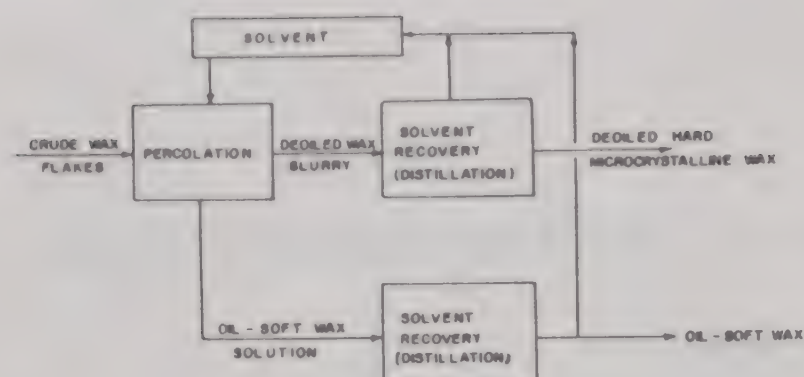


Fig. 1—Flow diagram for deoiling of microcrystalline wax flakes

The process flow diagram is shown in Fig. 1 and the results of the deoiling study are given in Table 2.

### Results and Discussion

Commercial microcrystalline wax, produced from Ankleshwar crude tank sludges in the form of flakes, has high oil content (11.2 per cent wt). Removal of the associated oil and soft wax from the wax flakes has been achieved by solvent percolation technique employing industrial hexane which was selected as deoiling solvent owing to its complete oil miscibility and relatively low solvent power for high melting wax constituents at ambient temperatures and easy recovery from product streams by distillation.

The results given in Table 2 show that hexane percolation through the wax flakes has reduced the oil content from about 11 per cent to below 2 per cent. Flash point and hardness of the product also improved due to separation of lighter contaminants from the feed stock.

The yield of the deoiled wax is about 74 per cent on feed. The wax has remarkably high melting point of 93°C and low needle penetration value of 4 at 25°C. Such waxes have considerable demand in domestic and international markets for paper converting, electrical insulation, polishes, carbon paper and melting point booster to other waxes.

The foot oil, obtained as a by-product in the process, has an oil content of about 50 per cent and melting point of 44°C. This may possibly be utilized in the formulation of technical grade petroleum jelly.

The technology, so developed, eliminates the need

Table 2—Yield and characteristics of the products

Operating Conditions		
Solvent/feed ratio, by wt	6/1	
Percolation column temperature, °C	28±2	
	Hard wax	Oil-soft wax
Yield, wt % on feed	74.2	25.8
Oil content, wt %	1.5	49.9
Melting point, °C	92.8	44.2
Needle penetration, d mm		
at 25°C	4	—
at 35°C	6	—
Kin. viscosity at 98.9°C	cST	14.23
Flash point, °C	268	170
Colour ASTM	1.5	2.5

of costly scraped surface crystallizers, rotary-drum filters and refrigeration equipment required in conventional solvent deoiling.

### Conclusion

The study shows that solvent percolation technique using industrial hexane could be employed for deoiling of high melting hard microcrystalline wax flakes. This route is particularly suitable for small capacity plants processing residual tank bottom waxes.

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## Structural feature of Boragolai coal (N.E. Coalfields) of India as derived from additive carbonization tests

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Coals from Boragolai coal mines of north eastern coalfields of India was carbonized both with and without additives, between the temperature ranges of 300-600°C. Effect of additives (such as  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{H}_3\text{PO}_4$ , ethylenediamine, and halogen) on the yields of pyrolysis products (coke, tar, liquor, and gas) along with temperature was thoroughly studied. Coke production was found to be highest with  $\text{ZnCl}_2$  indicating dehydrogenation of the hydroaromatic structure and since these coals contain very high amount of hydroaromatic moieties, the effect was great as compared to other Indian coals. Conversely, the results were in accordance with the reaction of mobile phase which is very large in such coals due to high V.M. content, and the additive reaction probabilities. The results were further corroborated by petrographic and pyrolysis studies. Addition of phosphoric acid, because of steric hindrance, results in minimum gas yield.  $\text{AlCl}_3$  on the other hand due to less severity and effectiveness towards aromatization of these large hydroaromatic moieties, produces minimum amount of coke. Large tar yields in later cases indicate that hydroaromatic structure must be present as side chain to the aromatic nucleus. Further, majority of the oxygen links in these coals were found to occur in between macromolecular aromatic moieties in favour of saturated ether cross links. Hydroaromaticity of the coal samples and treated samples were also determined by theoretical equations and relative values compared with experimental results. Present results of additive carbonization support modern view of two component coal structure - a mobile (predominantly aliphatic) molecular structure trapped within a three dimensional rigid cross-linked macromolecular structure. However, results of addition of  $\text{AlCl}_3$  contradicts above hypothesis, but supports dynamic macromolecular structural model of coal.

A large deposit of sub-bituminous, high caking coal occur in the north eastern region of India. These coals are of tertiary origin and contain low ash and high volatile matter. When we compare its fixed carbon content and volatile matter, its rank placement becomes difficult; thus it fits to matured bituminous coal on one ground and sub-bituminous coal on the other. These coals contain high amount of sulphur (about 4% by weight of total coal) and about 75-80% of this sulphur is organic in nature. Moreover experiments in our laboratory has shown that to break this organic sulphur, requires drastic conditions like strong alkali and high heat which indicates these organic sulphurs are mostly in thiophenic form (not in thiol or disulphide form). Abnormalities in the chemical properties of these tertiary coals of north eastern region of India and their sulphur distribution pattern in depth have been reported by Chandra *et al*<sup>1</sup>. Petrographic composition of this coal was determined by standard optical method<sup>2</sup> and the results are shown in Table 1. Additive carbonization with  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$ , halogens,

and sulphur was studied by Mazumder *et al*<sup>3-9</sup> with Gondwana coals of Bihar state (India), Bhattacharya *et al*<sup>10</sup> and Ganguly *et al*<sup>11</sup> both of CFRI, Dhanbad (India) studied pyrolysis behaviour of reduced coals and established experimentally that tar and gas yield is directly related to hydroaromatic structure of coal at 600°C and not to aromatic part of the coal sample. Studies on pyrolysis with  $\text{ZnCl}_2$  was also studied by Timothy *et al*<sup>12</sup>, Mobley *et al*<sup>13</sup> and Brienet *et al*<sup>14</sup> and established its distribution and catalytic effect during pyrolysis. Some NMR and IR studies of north eastern coals of India was also done by Rao *et al*<sup>15</sup> and a tentative structure for these coals were offered showing aromatic and alicyclic moieties clinging separately. The present structural concept of coal is based on two classes of components<sup>16</sup> - a molecular entity within which is trapped or clathrated inside a three-dimensional cross-linked macromolecular structure. Proton NMR investigation<sup>17-21</sup> of coal attributed Gaussian component of FID to macromolecular part having little rotational mobility while Lorentzian (mobile) proton according



to one school of thought<sup>22-24</sup> has been attributed to molecules that are free to rotate in cage of the macromolecular network and the other group maintains it due to fragments of the macromolecular network that can rotate. These are probably the hydroaromatic moieties observed by earlier workers<sup>3-9</sup>. These fragments would be linked to the network by a single C-C or C-O bond. A realistic approach to this controversy has been pyrolysis of the coal and identifying the loosely bound free molecules (e.g. by pyrolysis-field ionization mass spectrometry). The later studies with low rank bituminous coal (78% C<sub>daf</sub> at 500°C) & following NMR-Zeeman proton relaxation showed that about 32 wt% organic material in the coal represent its mobile phase. Additive carbonization, similarly, is expected to further substantiate above facts. Recent studies by Derbyshire & Davies<sup>25</sup> by fluorescence microscopy shows that the residual fluorescence remaining after extraction of the untreated coals was due to the presence of trapped mobile phase. Experiments by swelling coal with various solvents<sup>26-30</sup> has shown that these solvents increase the relative amount of the mobile component.

Aliphatic chains are probably more mobilized than the aromatic cluster. Studying along the same line Tekley & Delpuech<sup>31</sup> has shown that carbonization process at 590°C brings about a predominantly aromatic character of the mobile component. These structures are not extractable & therefore belong to, or remain with, the macromolecular network<sup>32</sup>. Narayan<sup>33</sup> has also shown from analysis of THF soluble fraction that the major aliphatic component of coal comprise of poly-ethylene -(CH<sub>2n</sub>)-groups. These low molecular weight polymethylene components may be present as trapped molecules. But Larsen<sup>34</sup> & Liotta<sup>35</sup> recently contradicted existence of separate mobile phase on the ground that non-covalent hydrogen bonds are the major important to network polymer structure which is possible only if we envisage a dynamic coal macromolecular structure composed of different molecular weight polymer chains, which give rise to a network structure due to chain entanglement, non-covalent hydrogen bonds, chelate bonds & other associative interactions. Under such controversy, we believe, additive carbonization with selective reagents may throw some light to the real fact. With similar thoughts, Schulten & Marzect<sup>36,37</sup> studied the reaction with pyridine, Takegami *et al*<sup>38</sup> & Whitehurst<sup>42</sup> with hydrogen, and Ignasik *et al*<sup>39</sup> through the reductive alkylation route. Several reports has recently been published<sup>40,41,43</sup> to establish the major linkages in these fragmented

structures and role of some hetero atoms, like oxygen, in forming ether linkages has been proved experimentally. While  $\alpha$ ,  $\beta$ -saturated cyclic ethers are found to be more reactive, the unsaturated cyclic ethers (such as furan) appear to be stable.

Looking at above state of our knowledge regarding structure of coal, present studies on additive carbonization was undertaken to augment above results and broadly elucidate structure of speciality coals found in the Boragolai mines of north eastern India. Additives were chosen on the ground that some are known to bring about aromatization & thus corroborate earlier experimental results while others participate in addition/elimination reaction and consequent change in pyrolysis product distribution pattern. Steric hindrance & consequent effect on pyrolysis products were investigated through incorporation of large anions in the additive chemical. Thus results of additive carbonization with ZnCl<sub>2</sub>, AlCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, ethylenediamine, and halogens with Boragolai coal is discussed below and its implication in favour and against of above available theories elucidated.

### Experimental Procedure

Coal samples for the present work were collected from Boragolai coal mine of Makum coalfield (Assam), India. Coals were carbonized in standard Gray-King assay apparatus (heating rate 5°C/min) from 300 to 600°C, both with & without additives. Additives such as AlCl<sub>3</sub>, ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, ethylenediamine, and chlorine was chosen for this purpose. These additives were added in 6-20% by wt. basis with the original coal samples. All coal samples were ground to -72 BS mesh size. In case of dry additives like AlCl<sub>3</sub> and ZnCl<sub>2</sub>, 20 gms of the additive was first dissolved in 50 ml distilled water and 100 gms of coal sample mixed with it in order to make it a homogeneous mixture; and in case of liquid additives (like phosphoric acid & ethylenediamine) coal samples were directly mixed with it and made into a homogeneous mixture. Water based coal-additive mixtures were dried in an oven at 110°C for 1 hour. Samples thus prepared with additives were then carbonized in G.K-assay apparatus by usual method and the pyrolysis products tar, liquor, and coke were estimated gravimetrically; gas was determined volumetrically. Final gas amount was determined by difference and the error in such case do not exceed 3 percent. Swelling index of the coal as well as for the coals with additives, are shown in Table 2. Swelling index was determined according to the standard procedure<sup>44</sup>.



Carbon and hydrogen content of all coal and coke samples were determined by standard absorption method (B.S.T.M) as described by Hunus<sup>45</sup>.

The coal samples, -200 BS mesh size, was chlorinated as follows. 40 gms of the dry ground sample was taken, in 250 ml of carbon tetrachloride in a round bottom flask fitted with condenser, gas purging inlet tube and a magnetic stirrer. The mixture was heated to reflux condition and chlorine gas bubbled through it while stirring the solution continuously. The mixture was saturated with chlorine in about 3 hours time and then cooled and filtered through Buchner funnel. The residue was washed with hot water (about 60°C) until chloride free & oven dried.

Proximate analysis (such as volatile matter content, moisture and ash) of all coal and coke samples were done by standard BSTM method<sup>46</sup>. Petrographic composition of the original coal sample determined by standard optical methods<sup>2</sup>.

Hydroaromaticity of the samples were determined from the carbon and hydrogen percentage as obtained above and using the equation proposed by Mazumder<sup>47</sup>. The equation as used by Ganguly *et al*<sup>11</sup> for both coal and semi-coke, was used here for hydroaromaticity determination for both coal & coke.

## Results and Discussion

Petrographic composition of the coal sample used in these experiments are shown in Table 1. As can be seen in above table, these coals contain a very large amount of vitrinite while exinite content is almost negligible. Proximate analysis of the coal sample is shown in Table 3. This table shows that the coal sample has a very high volatile matter content. Pyrolysis results with and without additives in the temperature range 300 to 600°C are shown in Table 4. Pyrolysis results (yield of coke/char, tar, gas, tar plus gas, and liquor) are plotted as function of temperature in Figs 1, 2, 3, 4 & 5 respectively. Proximate analysis of the corresponding coke/char obtained are shown in Table 3.

Hydroaromaticities of both coal and its carbonized products (coke/char) calculated based on the carbon and hydrogen ratio are shown in Table 5. Table 6 shows change in hydroaromaticity of coal on pyrolysis with different additives and also effect of temperature on such conversion. These results are shown graphically in Fig. 6.

A general form of thermogravimetric analysis result with these coals is shown in Fig. 7, which also depicts the comparative severity of the reactions with

Table 1—Petrographic analysis of Borogolai coal

Sample	Vitrinite (Vol.%)	Exinite (Vol.%)	Inertinite (Vol.%)	Mineral matter (Vol.%)
1 <sup>a</sup>	92.6	0.9	4.1	2.4

1<sup>a</sup> = Biorogolai coal

Table 2—Swelling index of coal sample with and without additives

Particulars of sample	Swelling index
Coal	6
Coal with 20% (by wt.) ZnCl <sub>2</sub>	1
Coal with 20% (by wt.) AlCl <sub>3</sub>	1
Coal with 10% (by wt.) H <sub>3</sub> PO <sub>4</sub>	0.5
Coal with 6% (by wt.) Ethylenediamine	5.5
Chlorinated coal	0

Table 6—Change in hydroaromaticity with additive and also with temperature

Sample	$\Delta f^*$ at 300°C	$\Delta f^*$ at 400°C	$\Delta f^*$ at 500°C	$\Delta f^*$ at 600°C
2 <sup>b</sup>	0.1	0.26	0.38	0.39
3 <sup>c</sup>	0.06	0.17	0.23	0.29
4 <sup>d</sup>	0.06	0.1	0.25	0.31
5 <sup>e</sup>	0.21	0.32	0.39	0.39
6 <sup>f</sup>	0.06	0.12	0.18	0.28
7 <sup>g</sup>	—	—	0.3	—

$\Delta f^* = f_{\text{har coal}} - f_{\text{har coke/char}}$  at different temperature

2<sup>b</sup> = Coal without additive

3<sup>c</sup> = Coal with 20% (by wt.) ZnCl<sub>2</sub>

4<sup>d</sup> = Coal with 20% (by wt.) AlCl<sub>3</sub>

5<sup>e</sup> = Coal with 10% (by wt.) H<sub>3</sub>PO<sub>4</sub>

6<sup>f</sup> = Coal with 6% (by wt.) Ethylenediamine

7<sup>g</sup> = Chlorinated coal

different additives. The figure also indicates a shift in maxima for weight loss towards lower temperature range occurring with these additives.

As can be noticed in Fig. 1, addition of ZnCl<sub>2</sub> suppresses the tar yield to the maximum extent as compared with other additives in present experiments and consequently gives rise to highest coke production, a result also recorded by Georgiadis & Gaillard<sup>48</sup>, and Bodily *et al*<sup>49-51</sup>. The latter author explained the phenomenon in the light of dehydrogenation of hydroaromatic structure during early stage of pyrolysis (200 to 400°C). No hydrogen was detected to evolve in case of untreated coal in the same temperature range. Similar effect of tar inhibition & dehydrogenation reaction was observed by Mazumder *et al*<sup>3-8</sup> with sulphur, selenium, and halogen. This phenomenon was found to relate with



Table 3—Proximate analysis of coal/coke/char

Sample	Pyrolysis temperature °C	% Moisture	% as received			Volatile matter (% dmf)	Fixed carbon (% dmf)
			Ash	Volatile matter	Fixed carbon		
1 <sup>a</sup>	—	1.72	3.45	43.7	51.1	46.2	53.8
2 <sup>b</sup>	300	1.36	2.22	42.4	54.1	44.0	56.0
3 <sup>c</sup>		1.3	2.1	40.5	56.1	42.0	58.0
4 <sup>d</sup>		2.0	6.12	39.3	52.6	43.1	57.0
5 <sup>e</sup>		1.57	2.13	41.5	54.8	43.2	56.8
6 <sup>f</sup>		3.02	5.75	36.7	54.5	40.5	59.5
2 <sup>b</sup>	400	2.78	1.96	24.0	71.3	25.2	74.8
3 <sup>c</sup>		2.01	2.5	27.8	67.7	29.2	70.8
4 <sup>d</sup>		1.55	7.02	40.3	51.2	44.4	55.4
5 <sup>e</sup>		1.6	2.74	32.5	63.1	33.5	66.5
6 <sup>f</sup>		1.86	5.6	26.8	65.8	29.1	70.9
2 <sup>b</sup>	500	2.65	2.75	24.9	69.7	26.4	73.6
3 <sup>c</sup>		2.4	2.6	22.6	72.4	23.9	76.1
4 <sup>d</sup>		2.59	8.33	20.4	68.7	23.1	76.9
5 <sup>e</sup>		2.2	4.13	15.9	77.8	17.0	83.0
6 <sup>f</sup>		2.06	5.99	16.9	75.0	18.5	81.5
7 <sup>g</sup>		3.12	2.98	43.7	50.1	46.7	53.3
2 <sup>b</sup>	600	1.38	3.22	18.1	77.3	26.4	73.6
3 <sup>c</sup>		1.45	3.1	18.5	77.0	19.5	80.6
4 <sup>d</sup>		2.91	5.61	9.12	83.1	10.0	90.1
5 <sup>e</sup>		1.9	3.5	12.5	82.1	13.3	86.7
6 <sup>f</sup>		2.69	7.72	14.6	75.0	16.5	83.6

1<sup>a</sup> = Borogolai coal sample; 2<sup>b</sup> = Coal without additive; 3<sup>c</sup> = Coal with 20% (by wt.) ZnCl<sub>2</sub>; 4<sup>d</sup> = Coal with 20% (by wt.) AlCl<sub>3</sub>; 5<sup>e</sup> = Coal with 10% (by wt.) H<sub>3</sub>PO<sub>4</sub>; 6<sup>f</sup> = Coal with 6% (by wt.) Ethylenediamene; and 7<sup>g</sup> = Chlorinated coal

the quantitative amount of hydroaromatic moieties by above authors. Comparing with other Indian coals<sup>9</sup> (refer to Table 5), present coals have comparatively large amount of hydroaromatic fractions or saturated chains, connecting aromatic macromolecular network. This is further illustrated by the proximate analysis and the high volatile content values in Table 3. Earlier works on reduced coals (Ganguly *et al*<sup>11</sup>) conclusively proved that yield of tar by pyrolysis at 600°C almost quantitatively relates to the hydroaromatic content of the parent coal. These results are further supported by pyrolysis of anthracite with ZnCl<sub>2</sub> (Ghosh<sup>52</sup>) which due to absence of hydroaromatic moieties do not produce any tar. Inversely, this cancels the possibility of any significant proportion of aromatic carbon converting to tar on pyrolysis. If we apply the present concept of coal structure (mobile molecular unit trapped in rigid cross-linked macromolecular network) it seems ZnCl<sub>2</sub> is effective in cyclizing aliphatics

polymethylene groups of the mobile phase. This is also indicated by high coke yield in this case. Further, lowest tar and highest gas yield indicates, oxygen present mostly in ether linkage between cross-linked macromolecular structure in these coals. Possibility for the occurrence of cyclic ether ( $\alpha,\beta$ -saturated type) is also more in this coal as the gas yield is high. Table 5 shows that H/C ratio, compared to original coal, increases with addition of above additive except for phosphoric acid. Probably this is due to decrease in aromaticity of coke at corresponding temperature upon addition of above chemical. Opposite effect has been noticed with the addition of phosphoric acid.

Among all additives tried in the present work, addition of phosphoric acid found to give minimum gas yield (see Fig. 3) but simultaneously increases tar yield when compared with other additives (Fig. 2). This is probably because large phosphate anions do not have access to trapped polymethylene molecular structure.



Table 4—Pyrolysis products at various temperatures

Sample	Pyrolysis temperature °C	Weight percent yield on dmf basis				
		Coke	Tar	Gas	Liquor	Tar and gas
2 <sup>b</sup>	300	94	3.4	0.84	1.7	4.24
3 <sup>c</sup>		95	Nil	1	3.9	1
4 <sup>d</sup>		86.5	Nil	0.73	12.7	0.73
5 <sup>e</sup>		92	1.5	0.47	6	1.97
6 <sup>f</sup>		91	2	0.6	6.4	2.6
2 <sup>b</sup>	400	78	14.85	4.38	2.7	19.23
3 <sup>c</sup>		81	9.5	6.63	2.85	16.13
4 <sup>d</sup>		75	10.45	2.7	11.8	11.15
5 <sup>e</sup>		76.5	11.5	2.5	9.5	14
6 <sup>f</sup>		77	13.2	3.08	6.7	16.98
2 <sup>b</sup>	500	72	16.5	8.3	3.2	24.8
3 <sup>c</sup>		76	11.2	9.5	3.3	20.7
4 <sup>d</sup>		67	12.1	6.98	13.9	19.08
5 <sup>e</sup>		69.6	13	7.5	9.9	20.5
6 <sup>f</sup>		70	14.5	8.0	7.2	24.5
7 <sup>g</sup>		71.5	5.5	7.1	16	12.6
2 <sup>b</sup>	600	65	18	13.4	3.6	31.4
3 <sup>c</sup>		69.4	12	15.1	3.5	27.1
4 <sup>d</sup>		60	13	11.9	15.1	24.9
5 <sup>e</sup>		61.5	15.5	11.5	11.5	27
6 <sup>f</sup>		64	16	12.5	7.5	28.5

2<sup>b</sup> = Coal without additive; 3<sup>c</sup> = Coal with 20% (by wt.) ZnCl<sub>2</sub>; 4<sup>d</sup> = Coal with 20% (by wt.) AlCl<sub>3</sub>; 5<sup>e</sup> = Coal with 10% (by wt.) H<sub>3</sub>PO<sub>4</sub>; 6<sup>f</sup> = Coal with 6% (by wt.) Ethylenediamine; and 7<sup>g</sup> = Chlorinated coal

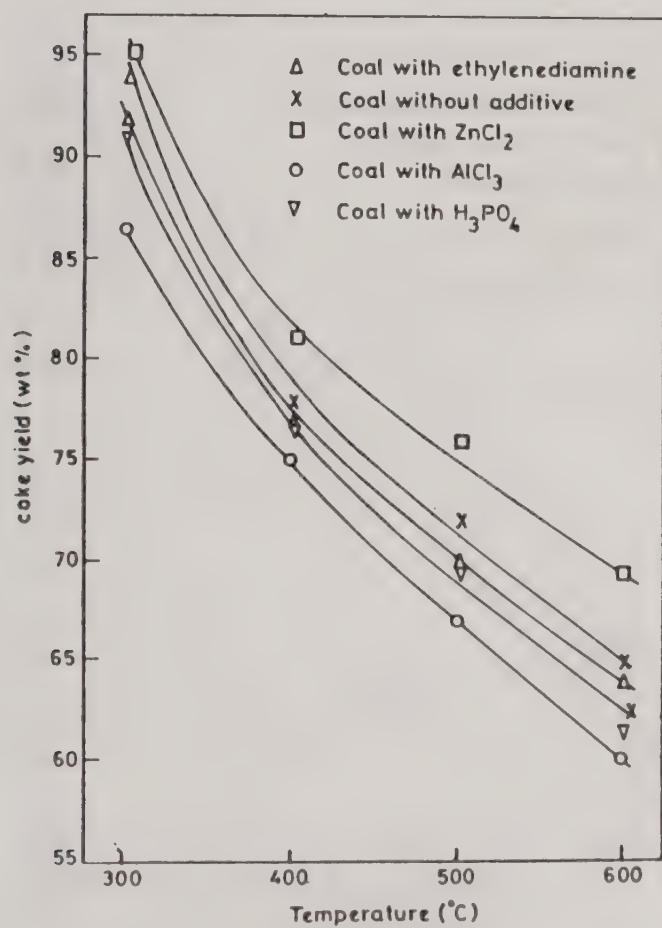


Fig. 1—Temperature versus coke yield

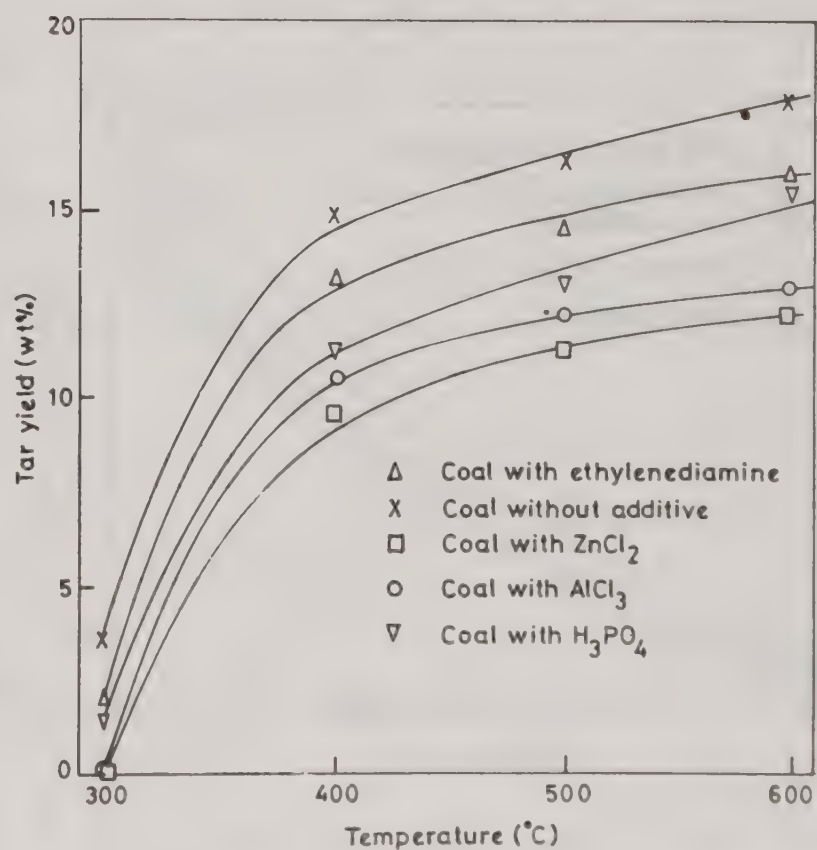


Fig. 2—Temperature versus Tar yield



Table 5—Carbon and hydrogen analysis of coal/coke/char (dmf basis)

Sample	Pyrolysis temperature °C	Percent carbon	Percent hydrogen	H/C	$f_{\text{har}}^*$	C:H
1 <sup>a</sup>	—	76.73	6.1	0.95	0.39	1.04:1
2 <sup>b</sup>	300	71.97	5.1—	0.85	0.29	1.2:
3 <sup>c</sup>		72.52	5.39	0.89	0.33	1.1:1
4 <sup>d</sup>		75.09	5.6	0.89	0.33	1.1:1
5 <sup>e</sup>		79.82	4.9	0.73	0.17	1.35:1
6 <sup>f</sup>		77.05	5.77	0.89	0.33	1.1:1
2 <sup>b</sup>	400	74.68	4.3	0.69	0.13	1.45:1
3 <sup>c</sup>		73.6	4.83	0.78	0.22	1.3:1
4 <sup>d</sup>		76.38	5.4	0.85	0.29	1.2:1
5 <sup>e</sup>		82.4	4.33	0.63	0.07	1.6:1
6 <sup>f</sup>		77.73	5.4	0.83	0.27	1.2:
2 <sup>b</sup>	500	77.7	3.71	0.57	0.01	1.75:1
3 <sup>c</sup>		75.15	4.54	0.72	0.16	1.4:
4 <sup>d</sup>		81.92	4.8	0.7	0.14	1.4:
5 <sup>e</sup>		85.64	3.8	0.53	Nil	1.9:1
6 <sup>f</sup>		79.36	5.1	0.77	0.21	1.3:1
7 <sup>g</sup>		78.3	4.3	0.65	0.09	1.5:1
2 <sup>b</sup>	600	81.51	3.17	0.47	Nil	2.1:1
3 <sup>c</sup>		76.62	4.2	0.65	0.10	1.5:1
4 <sup>d</sup>		82	4.36	0.63	0.7	1.6:1
5 <sup>e</sup>		88.9	3.39	0.45	Nil	2.2:1
6 <sup>f</sup>		83.87	4.7	0.67	0.11	1.5:1

$f_{\text{har}}^*$  = Hydroaromaticity; 1<sup>a</sup> = Borogolai coal sample; 2<sup>b</sup> = Coal with additive; 3<sup>c</sup> = Coal with 20% (by wt.) ZnCl<sub>2</sub>; 4<sup>d</sup> = Coal with 20% (by wt.) AlCl<sub>3</sub>; 5<sup>e</sup> = Coal with 10% (by wt.) H<sub>3</sub>PO<sub>4</sub>; 6<sup>f</sup> = Coal with 6% (by wt.) Ethylenediamine; and 7<sup>g</sup> = Chlorinated coal

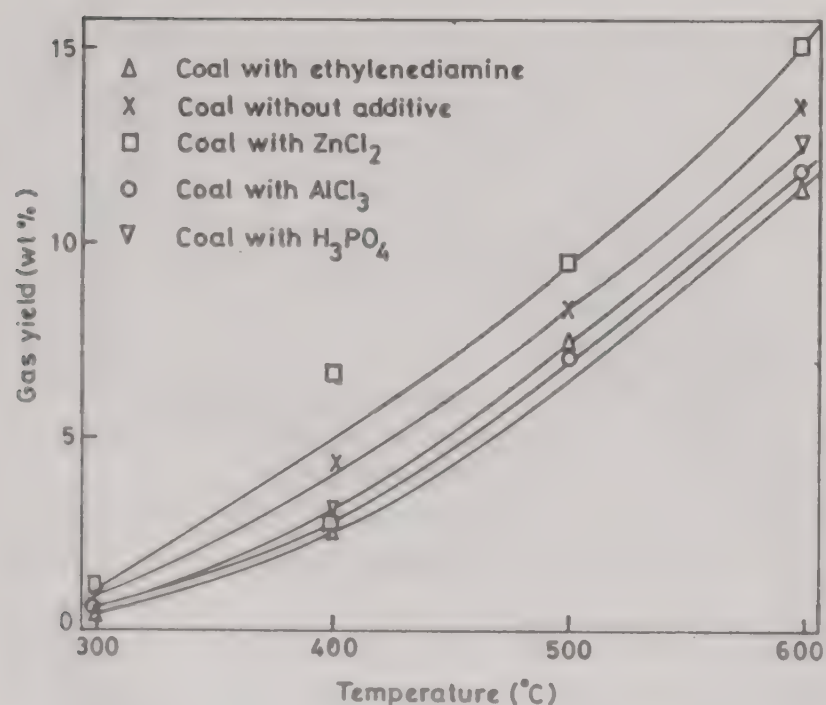


Fig. 3—Temperature versus Gas yield

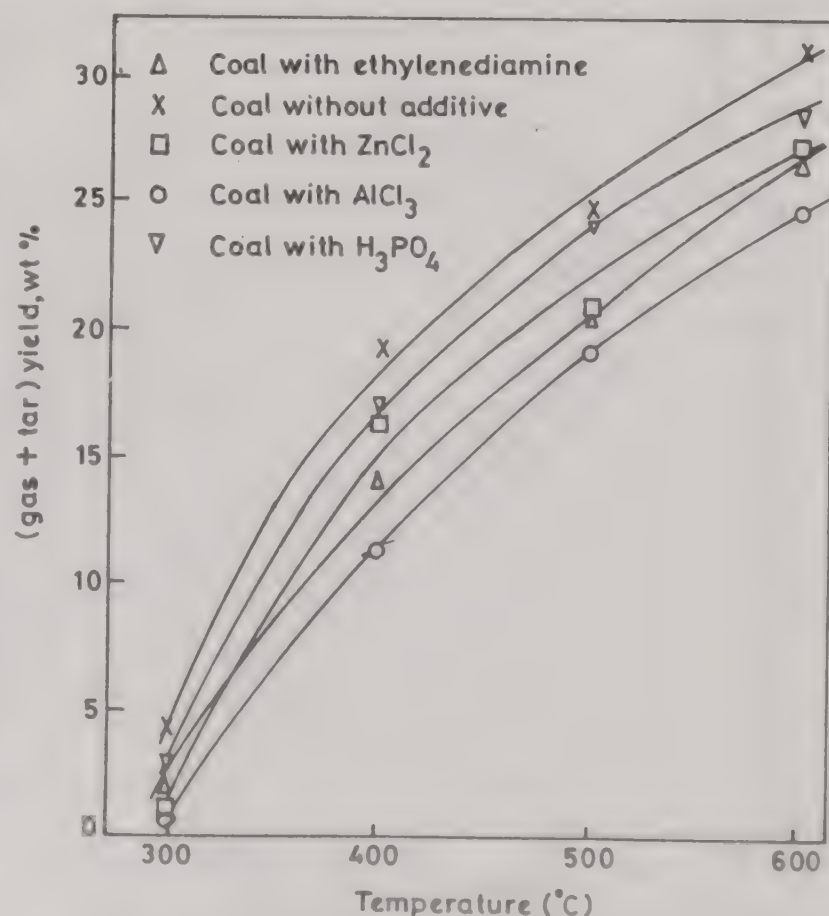


Fig. 4 Temperature versus (Gas + Tar) yield



Bodily *et al.*<sup>49-51</sup> by varying  $\text{ZnCl}_2$  concentration from 5 to 25% found that maximum stabilization of volatiles (100% suppression of tar formation) takes place at about 20% loading of  $\text{ZnCl}_2$ , accordingly we decided to use 20%  $\text{ZnCl}_2$  addition in all our reactions to compare the large changes. It was also found by above authors that for both higher and lower rank coals most of the dehydrogenation reaction takes place at lower temperature (below  $400^\circ\text{C}$ ) resulting in a large volume of gas emission; subsequently change in tar yield and increase in char production attributed to this lower temperature reaction. Virtually a similar observation was found with sulphur and halogen by Mazumder<sup>53</sup> where change in pyrolytic behaviour in the same fashion observed along with near suppression of tar formation and increase in char yield. In the present experiments highest increase in char was also observed with  $\text{ZnCl}_2$  addition (Fig. 1).

Figures 1 and 3 indicate that production of tar with  $\text{AlCl}_3$  is more than  $\text{ZnCl}_2$  and thus the severity of reaction with  $\text{AlCl}_3$  is less and the same pattern follows from thermogravimetric analysis (Fig. 7). Mazumder *et al.*<sup>9</sup> found similarity between Scholl's

reaction ( $\text{AlCl}_3$  with coal in presence of  $\text{NaCl}$ ) at  $120-130^\circ\text{C}$  and  $\text{ZnCl}_2$  reaction at low temperature (below pyrolytic conditions). In this case addition of  $\text{AlCl}_3$  alone thus do not improve production of coke compared to other additives (in fact it yields lowest amount of coke during pyrolysis, indicating ineffectiveness of the additive in aromatizing large hydroaromatics moieties in such coals). Tar and liquor obtained by carbonization with  $\text{AlCl}_3$  was found to contain large amount of phenol and swelling index of coke was also found to decrease as compared to original coal. It should be noticed in Table 4 that liquor yield with  $\text{AlCl}_3$  is abnormally high in all temperature range. From mass balance point of view it is also seen that with  $\text{AlCl}_3$  addition, coke production with  $\text{AlCl}_3$  is minimum among all additives tested but tar yield do not increase proportionately and thus the liquor yield (which is

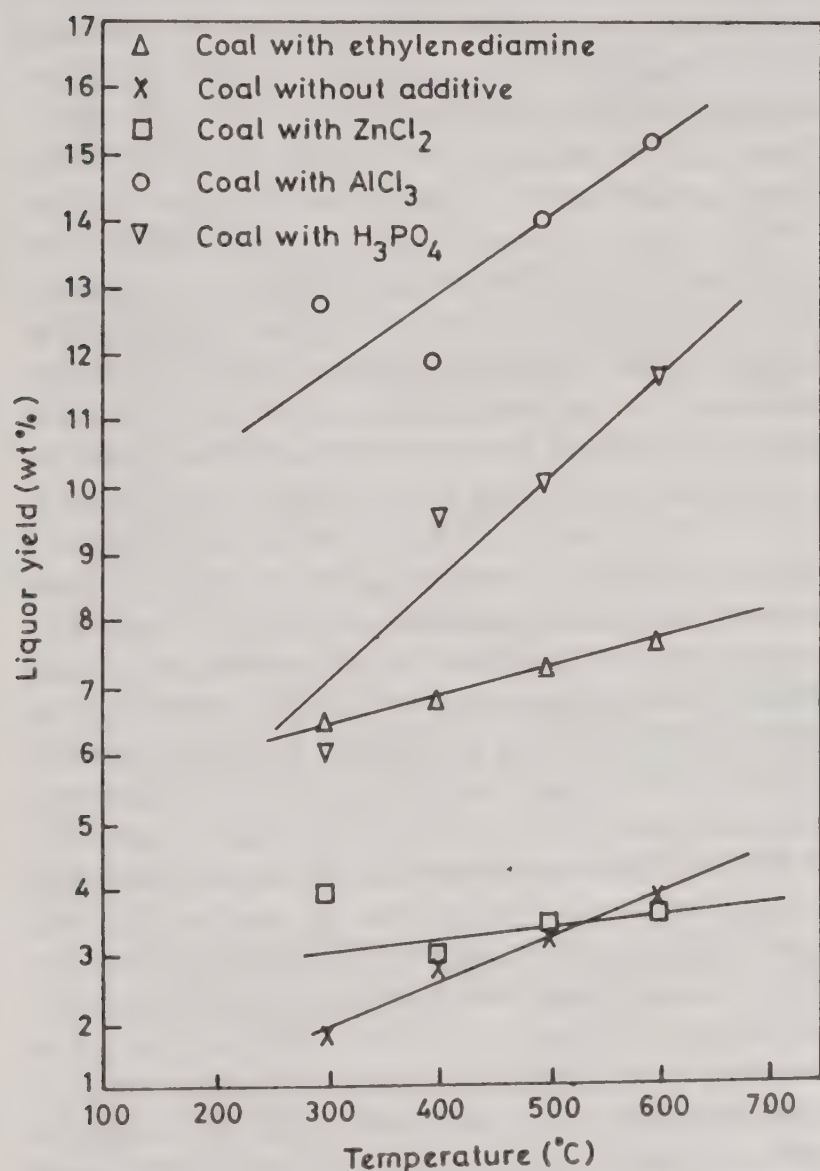


Fig. 5—Temperature versus liquor yield

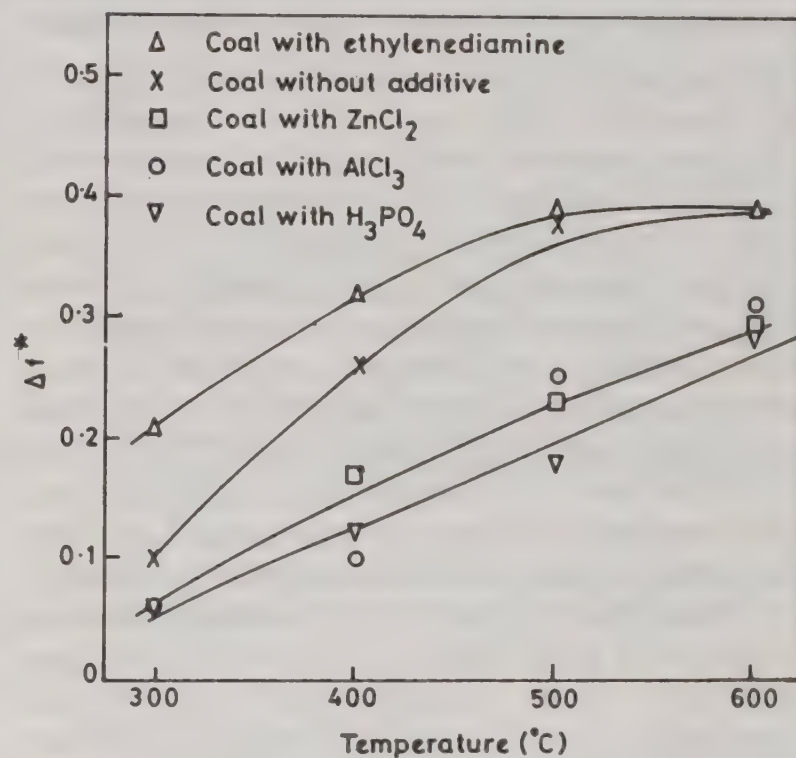


Fig. 6—Temperature versus change in hydroaromaticity ( $\Delta f^*$ )

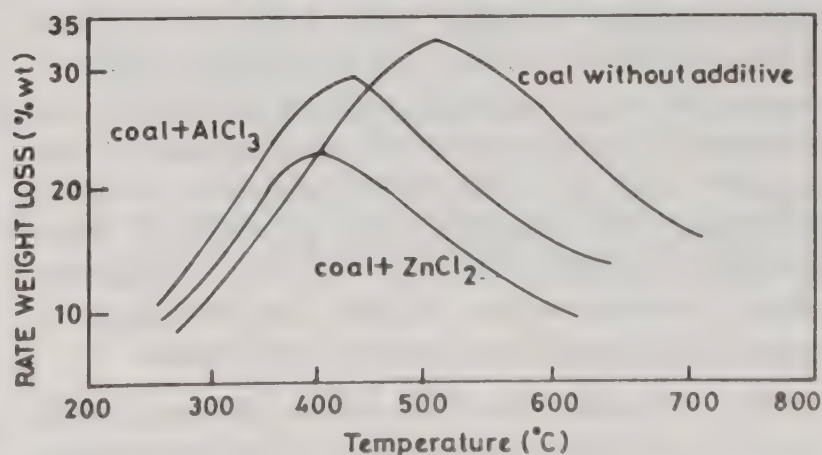


Fig. 7—Temperature versus rate weight loss



high in phenol & water) is increased to a great extent. Similarly with  $\text{H}_3\text{PO}_4$  addition, liquor yield also is high and the pH was found acidic (2-6) in the temperature range studied. In later case, liquor yield was also found to be highly sensitive to temperature change (as can be seen from Fig. 5, the highest gradient line) while coke and tar yield is moderate. This coal thus seems to have most of its oxygen in etheral linkage between macromolecular phases and available for  $\text{AlCl}_3$  reaction. This also indicates absence or presence of at most very small amount of unsaturated cyclic ethers in these cross-links.  $\text{AlCl}_3$  in all such cases brings about elimination reaction with oxygen (as  $\text{H}_2\text{O}$ ) rather than condensation and consequent ring growth. This occurs probably due to rigidity of the macromolecular phase. Further, Table 3 shows that  $\text{AlCl}_3$  reaction is prominent with mobile phase (volatile matter of the coal) and thus this phase must be present outside the rigid, macromolecular structure as against the continuous chain structure hypothesized by some workers and mentioned earlier. Swelling property was also found to be destroyed to the maximum extent with these two additives, indicating vigorous reaction of the additives with external hydroaromatic moieties and oxygen cross-links. As mentioned by Mazumder<sup>54</sup> that in such reactions hydroaromatic part changes to some reorganization and apparent condensation reaction with aromatic part takes place not only through dehydrogenation reaction but also a host of other reactions results in high liquor yield. Thus in this particular coal, as was found by above author, hydroaromatic structure must be present as a side chain and as cross-links between macromolecular moieties and carrying most oxygen and functionalities in saturated ether links to the aromatic nucleus (otherwise from stereochemical view point occurrence of such reaction would be a remote possibility) and thus cyclo-dehydrogenation and/or cyclisation reaction becomes feasible. Thus the present results contradicts the present day two phase theory on the ground that if  $\text{AlCl}_3$  reacts with predominantly aromatic stationary cross-linked macromolecular structure, one would expect a higher coke yield but as shown above, opposite results are obtained. The experimental results thus found supports rather Narayans<sup>33</sup> dynamic macromolecular coal structure and presence of non-covalent hydrogen bond in the macromolecular phase. Hydroaromatic moieties thus envisaged as cross links between macromolecular phases.

Yield of gas was found to be lowest in case of  $\text{H}_3\text{PO}_4$  addition; indicating association of hydroaromatic moieties and consequent thermal stabilization of the

product. As can be seen from Fig. 1, addition of  $\text{H}_3\text{PO}_4$  also suppresses tar formation but not as much as  $\text{ZnCl}_2$  or  $\text{AlCl}_3$ . Swelling property of the coal was also found to be totally destroyed by addition of  $\text{H}_3\text{PO}_4$ . Phosphate anions in such case was ineffective in breaking the bond in macromolecular structure but participate in various addition reactions in unsaturated sites (most probably at oxygen cross links).

Carbonization of the chlorinated coal (sample number 7<sup>e</sup>) do not produce chlorinated tar but HCl. Volatile matter and fixed carbon contents of the sample before and after carbonization was found to remain almost same (at  $500^\circ\text{C}$ ). Tar yield in such case was also found to reduce drastically while liquor production increased considerably. Thus it seems chlorine in such coal promotes condensation and molecular growth through elimination of hydrogen-halide rather than degradation reaction found with other additives. The effect is quite pronounced as the hydroaromatic content is high in this speciality coal.

Addition of ethylenediamine increases swelling property of this coal and produces highly porous coke. While fumes were observed to emanate around  $170^\circ\text{C}$  associated with evolution of ammonia gas. Swelling at early stage of pyrolysis is probably due to formation of chelate type complexes with EDA, which subsequently at higher temperature (above  $15^\circ\text{C}$ ) breaks down giving rise to  $\text{NH}_3$  and simultaneously causes extensive porous structure in the carbon skeleton at the time of escaping through it. Data in Table 5 indicate that there is almost complete retention of carbon in char in all pyrolysis experiments done with above mentioned additives and, in fact, there was enhancement of percent C content in char with addition of phosphoric acid and ethylenediamine. These additives thus seem to bring about same reorganization in aromatic-hydroaromatic skeletal structure of this speciality coal and thus lead to stabilization and retention of both type of carbon in char during subsequent pyrolysis (note in Table 5 that with additives at corresponding temperatures hydroaromaticity is higher). Addition of EDA increases accessibility of the reagent to the trapped molecular phase due to swelling of coal matrix and since this coal has high volatile matter (i.e. more mobile phase) the effect is quite pronounced as can be seen in Figs 1, 2, and 3. EDA is effective in breaking small fragments, after addition reactions, from molecular phase and increases both tar and gas yield with increase in the pyrolysis temperature; while resultant coke yield from rigid macromolecular phase remains more or less constant.



## Conclusion

Finally, it is interesting to note that since these speciality coals have higher hydroaromatic content (less %C and higher %H) compared to other Indian coals<sup>9</sup>, effect of the additives tested in these experiments are quite high (see Table 6 and Fig. 6 showing changes in hydroaromaticity with the additives along with increase in temperature). In fact, a linear relation between change in hydroaromaticity ( $\Delta f^*$ ) and temperature was found in all these additive carbonization tests. It is also to be noted that these coals contain high percentage of sulphur (3.1% in this particular coal) of which most sulphur is in organic thiophenic form (reasons mentioned earlier). These thiophenic rings in presence of  $ZnCl_2$  further helps in addition reactions to phenyl or aliphatics chain (as in Fisher synthesis). Thus presence of sulphur in this coal promotes condensation reaction and brings about higher coke yield with this additive. Conversely, it may be assumed that sulphur like oxygen is mostly present in the mobile phase and also associated in cross-links with macromolecular entities. Above results thus, in conclusion, supports basic aromatics structure of coal connected by hydroaromatic moieties and at the same time establishes existence of a mobile phase available within large aromatics and relatively stationary macromolecular phase.

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## Technology Up-date

### **New software to make products servicing easy**

*Design News*, 49(5) (1994) 44

Ford, Navistar, Digital Equipment Corporation, and DuPont are among the companies planning to use new software to make their products easier to service.

Design for Service (DFS), developed by Boothroyd Dewhurst Inc., enables users to consider potential service problems, costs, and solutions while they are still in the conceptual phase of product design. The software, integrated with Boothroyd Dewhurst's Design for Assembly (DFA) programme, runs on personal computers under Windows.

According to company co-founder Peter Dewhurst DFS may play a significant role in the next competitive battle for consumers' mind share. People are increasingly disenchanted with the difficulties of service for many products, and with environmental and cost issues becoming more important to everyone, the marketing value for manufacturers of DFS-driven products is quite clear.

The integration with DFA means that engineers can use existing data, such as parts consolidation, parts lists, and assembly times and costs. Users identify each service item and choose a disassembly sequence. The software automatically generates a reassembly sequence. The finished analysis includes a worksheet of service tasks with estimates of total disassembly and reassembly times, a serviceability rating index, and identification of serviceability costs, such as labour, operation, part, and replacement costs.

Price for the software will be \$ 14,500 per seat.

### **Polyethylene car seat for large children**

*Design News*, 49(5) (1994) 51.

Using a rotational molding process, Snug Seat Inc., of Matthews, and First Function, of Raleigh, NC, have designed a polyethylene car seat for large children. The seat passes the Canadian Motor Vehicle standard for seats that safely accommodate children up to 105 lbs.

Traditional car seats for children up to 50 lbs usually consist of a plastic shell and metal frame, but that design doesn't scale-up well for larger children. To solve that problem, the companies originally

designed a vacuum-formed shell with an egg-crate-style honeycomb reinforcement ultrasonically welded on the back. While it was stiff enough, the wind portions weren't strong enough.

The polyethylene material has a wall thickness of 3/16 inch. A variety of molded-in-slots accommodate the straps and belts and help secure the padding. The slots stiffen the structure by connecting the two surfaces. In areas where there are no slots, several blind holes to stiffen the structure are used.

To accommodate a child's growth, a U-shaped extension attaches to the front of the seat with screws.

Zwick Engineering, Elkin, NC, produced the tooling, and Accuform Polymers, Wendell, NC, molds the parts.

### **Resistivity meter for strength monitoring of concrete**

The Central Electrochemical Research Institute (CECRI), Karaikudi, has developed a four probe resistivity meter for non-destructive monitoring of the strength of concrete. It is a portable, battery-operated instrument for surveying the condition of RCC bridges.

It consists of a built-in spring-loaded four-probe unit and a sophisticated electronic circuitry and displays the current-voltage data in terms of resistivity through a liquid crystal device. The tips of the four electrodes are wrapped with sponge saturated with potable water, for making effective contact with the concrete surface.

Two units of the instrument were recently handed over to M/s Hooghly River Bridge Commissioner, Calcutta, and M/s Associated Cement Company, Thane.

Further details regarding the instrument can be had from the Director, CECRI, Karaikudi 623 006.

### **New hydrophilic acrylic fibre**

Pasupati Acrylon Ltd, New Delhi, in association with the Department of Textile Technology, IIT, Delhi, has developed a new hydrophilic acrylic fibre. This high performance fibre has been specifically developed keeping in view the specific needs of the Indian climatic conditions. The new fibre has all the positive attributes of acrylic coupled with the moisture absorption properties of cotton. It would



find extensive usage in T-shirts, sports wear, track suits, polo shirts, socks and speciality towels. Garments made out of this fibre will be available in a wide variety of bright un-fading colours, durable, not affected by moth and insects, light in weight, soft to the hand and extremely easy to wash and manage. They would breathe as cotton garments and in addition would have an excellent moisture absorption and transport property which would help take away the sweat from the body and keep it dry.

The hydrophilic fibre made by Pasupati has a microporous structure which is obtained by conjugate spinning of poly acrylonitrile with a cellulose derivative. The cellulose derivative gets distributed in an elongated form having its longest dimension parallel to the fibre axis. The resulting phase separation in the two leads to development of voids. These micro voids are distributed both in core and sheath. This provides the fibre with enhanced water absorption and rapid capillary action and thereby faster moisture transport.

Although the fibre has a microporous structure it has depicted good tensile properties. Table 1 gives the comparative characteristic of hydrophilic acrylic fibre against normal acrylic fibre and cotton.

Extensive work has been done by the company in developing towels and knitted fabrics out of the hydrophilic acrylic fibre. The results are in Table 2.

It was established that these towels have an excellent absorption and in addition to that can dry very quickly. They are extremely durable and have excellent colour fastness. These towels unlike cotton towels remain soft on repeated washes. Tests conducted on knitted fabric have been yielding equally good results.

This new hydrophilic acrylic fibre introduced by Pasupati Acrylic Ltd is the fibre most appropriate for

Table 2-Towel characteristics

S.No.	Sample particulars	Acrylic hydrophilic towels	Cotton towels
1.	Water absorbed	768%	525%
2.	Comparative drying		
a.	Water retained on soaking for 30 sec and squeezing	169%	243%
b.	Water retained in sample a after 1 hr. drying in ambient temperature	106%	186%
c.	Residual water in sample a after 2.5 hr drying in ambient temperature	6%	62%
3.	No. of cycles required to rupture the towel	1035	469
4.	Washing fastness		
a.	Change in shade	4/5	4
b.	Staining on white cloth	4/5	4
5.	Crock fastness		
a.	Dry	5	5
b.	Wet	4/5	4/5

the climatic conditions prevailing in tropical countries.

For further details contact Professor P Bajaj, Department of Textile Technology, IIT, Delhi, or Mr M Dara, Pasupati Acrylon Ltd, M-14, Connaught Circus (Middle Circle), New Delhi 110 001.

### High-temperature superconducting film

*Chem Eng News*, 72(11) (1994) 24

Researchers have succeeded for the first time in preparing thin films of a mercury-containing cuprate that show good high-temperature superconducting properties. Mercury cuprates that become superconducting at temperatures above 130 K were discovered earlier, but it has proven to be extremely difficult to prepare thin films of these superconductors because of the highly volatile nature of mercury and mercury-containing starting materials such as HgO. That problem now seems to have been solved by Chang C Tsuei and coworkers at IBM Research Division's T J Watson Research Center in Yorktown Heights, NY. They developed a pulsed-laser technique for depositing sequential layers of HgO and Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub> from two separate targets, resulting in atomic scale mixing of the elements at room temperature. The laser-deposited films are then annealed at up to 800°C to form the superconducting phase, HgBa<sub>2</sub>CaCu<sub>2</sub>O<sub>6+δ</sub>. A protective oxide coating deposited on top of the cuprate film also helps retain mercury during the

Table 1-Characteristics of various fibres

Characteristics	Normal acrylic fibre	Hydrophilic acrylic fibre	Cotton
Denier	1.5	1.5	1.5
Tenacity	3.0-3.5	2.8-3.0	2.1-3.0
%Elongation at break	35-40	26-30	3-10
% Water absorption	3-5	25-35	35-45
Density	1.17	1.10	1.54
Capillary action	poor	excellent	good
Drying capacity	excellent	very good	good
Dyeing properties	very good	very good	good



annealing step. The resulting films exhibit zero resistance at 124 K and can carry a current of 50,000 amp per sq.cm. at 77 K.

#### **Know-how for high set remote prop**

The know-how for high set remote prop developed by the Central Mining Research Institute (CMRI), Dhanbad, has been recently released through NRDC to M/s PVR Inshield Bituminous Private Limited, Burdwan, for commercial exploitation.

The prop developed can be used as an immediate front roof support (IFRS) and goaf-edge support in underground mines. It has high axial load (40 tonnes) bearing and setting load (10 tonnes) capacity with built-in-remote withdrawal device to be pulled by a tirfor from any distance. The setting device is a handhold twin jack with light hand pump. The telescopic range of the prop is from 600 to 1000 mm. It can be dismembered into two parts for easy transportation.

#### **High-temperature superconducting cable**

*Design News*, 49(5) (1994) 30

American Superconductor Corporation (ASC) has successfully tested a high-temperature superconducting cable and supplied the wire coils for a 5-hp superconducting motor.

The 1-metre prototype cable ACS tested carried 2,300 A of direct current when cooled to 77 K (-321 F) by liquid nitrogen. This current level is more than twice ASC's previous record of 1,100 A. The 2,300 A also exceeds the 2,000 A maximum current rating determined by the industry-funded Electric Power Research Institute (EPRI) for commercial high-temperature-superconductor power-transmission cables. Such superconducting cables could replace existing underground copper cables and carry twice the power with virtually no losses.

According to ASC president Greg Yurek, results on the 1-metre-prototype cable conductors and on wires hundreds of metres long show that high-temperature superconducting wires can achieve performance required for commercial applications.

ASC designed the prototype cable with Pirolli Cable SpA, Milan, Italy. The companies have collaborated over the last four years to develop high-temperature-superconductor wires for power transmission.

ASC has produced a 600 m superconducting wire with a current density of 70,000 A/cm<sup>2</sup>. It hopes to make a 1,000 m wire this spring.

Cleveland-based Reliance Electric tested a superconducting motor having rotating

high-temperature-superconducting coils from ASC. The ac motor's four racetrack-shaped coils had a total wire length of 670 m. The coils rotate at 1,800 rpm, delivering an output power of 3,730 W, or 5 hp.

The rotating-field synchronous motor uses the same type of construction the company plans for 1,000-to 10,000-hp motors for industrial and electric utility applications.

#### **Synthesis of industrial chemicals with visible light**

*European Chem News*, 61(1615) (1994) 39

A Research team in California has succeeded in harnessing visible light at ambient temperatures to effect the syntheses of a number of industrially important small molecules.

Heinz Frei and colleagues at the Lawrence Berkeley Laboratory have already succeeded in achieving selective photo-oxidation of toluene to benzaldehyde, propylene to acrolein and *cis*- and *trans*-butenes to the corresponding alkene hydroperoxides all reactions of considerable industrial interest. Their technique could be extended to a whole range of other chemical syntheses starting from small olefins and aromatics.

Key to the scientists success is to carry out the hydrocarbon/oxygen reaction in a barium or calcium exchange zeolite. The high electrostatic field in the zeolite cage stabilises the excited charge transfer states. This brings the absorption band from the UV into the visible, even into the red. The advantage of performing reactions in the visible or near-IRS is that the mild conditions lead to selective oxidation, avoiding the breakdown products synonymous with UV irradiation. The use of visible light is also comparatively cheap.

Frei is particularly interested in alkene hydroperoxides because of the important role of hydrocarbon hydroperoxides in industrial epoxidation reactions. Frei has discovered that, during the photo-oxidation of *cis*- and *trans*-butenes to the corresponding alkene hydroperoxides, the alkene hydroperoxide epoxidises, any excess *cis*- or *trans*-butene under complete stereochemical retention. As a result, the reaction holds promise as a means of carrying out industrial epoxidations *in situ*.

To date, all work remains on the laboratory scale. However, according to Frei, all the parameters and results obtained are 'encouraging' and is keen to follow up practical applications. Though yet to win industrial backing to scale up the work, he reports considerable interest from a number of US and European companies.



### **Nondetergent process for cleaning contact lenses**

*New Sci*, 142(1922) (1994) 20 &  
*Chem Eng News*, 72(12) (1994) 24

A way to clean soft contact lenses without the detergents that can irritate eyes is being developed from a method used to transfer proteins in laboratory studies. According to scientists at North Carolina State University, the technique, called electro-blotting, cleans lenses thoroughly using just a trickle of electric current, blotting paper and saline solution.

This process may enable people who are allergic or sensitive to cleaning agents to wear contacts. It is developed by science and biochemistry professor Harold E. Swaisgood and coworkers.

Electro-blotting was developed to transfer proteins from a porous gel onto blotting paper. Protein molecules carry an electrical charge, either positive or negative, so in the presence of an electric field the molecule moves with a mobility proportional to the size of its charge. For cleaning lenses, which become coated with proteins from the wearer's tears, electro-blotting causes proteins to migrate from the lens into wet blotting paper placed over both sides of the lens. In just four hours, almost all the deposits on a lens migrate onto the paper, which is then discarded.

Electro blotting removes 94.42 per cent of the protein. Hand-washing with a commercial cleaner removed 86.87 per cent. For anyone allergic to the detergent, electro-blotting would be a useful alternative. The process was developed for soft lenses, but is potentially applicable to hard lenses as well. Salem Products Development of Winston-Salem in North Carolina, is testing a prototype lens cleaning device. The final kit could be on sale within three years and cost less than \$100.

### **Solar pond technology commercialised**

Asia's first solar pond for water heating in a dairy plant at Bhuj (Gujarat) has been dedicated to the nation. This is going to be one of the most promising technologies in solar energy utilization to process heat, power generation, desalination, crop drying, and refrigeration in the country.

The thermal energy generated from the pond is being used to heat 80,000 litres of fresh water every day to 70 degree Celsius. A solar pond is a large scale solar energy collector with integral heat storage for supplying thermal energy. This thermal energy can be used in various ways such as process heating, water desalination, refrigeration and drying.

Here is how a solar pond works. Fluids such as water and air become lighter and rise when heated. This phenomenon makes flying of hot air balloons possible. Similarly, on an ordinary day, when the

sun's rays heat up the water, the hot water from the bottom of the pond rises, reaches the surface and loses whatever heat it has gained, to the atmosphere. The net result is that the pond water remains at nearly atmospheric temperature.

The solar pond technology inhibits this tendency of heat loss through convection. This is achieved by dissolving salt into the bottom layer of the pond, making it too heavy to rise, even when hot, to the surface and cool.

A pond consists of three zones. The top zone is the surface zone, which is at atmospheric temperature, and has little salt content.

The bottom zone is very hot between 70 to 100 degree Celsius and very salty, with specific gravity of about 1.20. It is this zone which collects and stores the solar energy in the form of heat and hence it is known as the storage zone.

Separating these two zones is the important gradient zone. This gradient zone acts as a transparent insulator, permitting sunlight to reach the bottom zone and its thermal energy to remain entrapped there. The useful energy is then withdrawn from the solar pond in the form of hot brine from the storage zone.

The solar pond has got three major advantages over other solar technologies. Firstly, they have a low cost per unit area as the collectors have an in-built large storage capacity. Secondly, they can be constructed over large areas enabling the diffused solar radiation to be concentrated on a large scale. Thirdly, they can supply energy even during the monsoon season.

The Bhuj solar pond project is a R&D and demonstration project of the government, at a total outlay of Rs 87.3 lakh (ET, 1.6.94).

### **New technique for sterilization of black pepper**

A thermal processing technique for the sterilization of whole black pepper to reduce the microbial load to permissible levels to the importing countries has been recently developed and standardized at the Mysore based Central Food Technological Research Institute (CFTRI). The product thus obtained is clean, glossy, bold and sterilized. The flavour characteristics, i.e. volatile oil, resin and piperine are not at all affected. This patented process would help further improve the export potential of the Indian black pepper.

In this process, commercially acceptable quality black pepper is subjected to air classification, destoning, garbling and such other operations of cleaning and grading. The cleaned black pepper is then passed through a wet heat process system under



standardized conditions for a specific time. It is then dried in hot air prior to packing in a closed system. The machinery required for this process are standard equipment indigenously available in the country.

#### **Technology for manufacturing coffee concentrate**

The Central Food Technological Research Institute (CFTRI), Mysore, has developed technology for manufacturing coffee brew concentrate in liquid form, which lends greater convenience to the consumers. The quality of coffee prepared from this is found to be superior to the filtered brew. It has good market potential with wider scope for being used in hotels and other catering establishments.

The process consists of selection of raw coffee seeds, roasting and grinding to coarse power which can then be wetted and extracted in jacketed percolater with hot water. The coffee brew is then stored in glass bottles under carbon-dioxide atmosphere.

The equipment needed are indigenously available and include mainly the coffee roaster, grinder, extractor and bottling unit.

The product is an ideal substitute for instant coffee (hot as well as cold) and as an intermediate product for coffee flavoured confectioneries.

#### **Efficient process for making formic acid**

*Chem Eng News*, 72(12) (1994) 21

An efficient process has been devised by Philip G Jessop, Takao Ikariya, and Ryoji Noyori at Research Development Corporation of Japan, in Toyota, Japan, for making formic acid by hydrogenation of super critical carbon dioxide (CO<sub>2</sub>) heated above its critical point (3°C and 73 atm), at which gas and liquid

CO<sub>2</sub> merge into a single phase. use of CO<sub>2</sub> as a starting material for industrial synthesis of formic acid and other organic compounds has been of long-standing interest for commercial and environmental reasons. It leads to a high initial reaction rate of 1,400 moles of formic acid produced per hour per mole of catalyst almost five times as fast as a similar formic acid synthesis in water reported earlier by Walter Leitner and Franz Gassner of the Max Planck Society, Jena, Germany. The concept of using supercritical CO<sub>2</sub> as both solvent and reactant was first demonstrated by Manfred T Reetz, Werner Konen and Thomas Strack of the Max Planck Institute for Coal Research, Mulheim, Germany.

#### **Technology to manufacture pomegranate products**

The Central Food Technological Research Institute (CFTRI), Mysore, has developed a technology package to manufacture a wide variety of delicious products from pomegranate, a highly valued fruit generally consumed fresh. Pomegranate can be processed to yield delicately flavoured beverage and delicious mixed fruit drinks by blending with other fruit juices. It is also possible to prepare good quality squash. Pomegranate jelly can be used like any other fruit jelly, as a spread.

Soft-seeded or seedless pomegranate variety is preferred for processing and preparing the products. The processing involves cutting open of the fruit, rain separation and pressing in screw press to obtain juice. The juice is then suitably treated, filtered and thus clarified. Sweetened juice is then prepared with 85 per cent clarified juice, squash with 40 per cent juice and RTS beverage blends with 25 per cent juice content. In jelly, the fruit content is 45 per cent.



## Techno-economic News Round-up

### **IIP's contribution in lube refining industry**

IIP has made significant contributions to the development of lube refining industry in our country. Starting with the creation of research facilities to evaluate crudes for their capability to yield LOBS, the Institute has gone up to process development and speciality lubricants. In fact, IIP was deeply involved in the development of design basis of Haldia lube complex by participating in the experimental work carried out in Romania and process design of MRL lube plants by AMOCO in USA.

Over the years, IIP has screened and evaluated nearly 40 crudes both indigenous and imported, for their lube base stock potential and processing behaviour. Large number of such studies have provided technological backup to the operating lube units.

IIP has also carried out extensive studies on the characterization of base oils of various viscosity and pour levels with changes in degree and type of refining using adsorption chromatography, IR, NMR and mass spectroscopy. The data generated have been used in property correlations and establishing inter-relationships between structural parameters and response of additives; pour point depressants and oxidation inhibitors in different series of base oils, some of which have been published in international journals.

Notable recent success achieved is the development of NMP base lube extraction process in collaboration with the R&D centres of Engineers India Ltd and Madras Refineries Ltd. Extensive process development efforts have been translated into the near commercial reality with the acceptance of this process for the change over of phenol extraction unit at Barauni Refinery with the newly developed NMP base process, preparation of process package for which is in the final completion stage.

IIP has also looked into the possible application of 'hybrid' technology, combining the use of solvent extraction and mild hydrotreating by way of studies for an operating refinery. Experimental studies have confirmed the techno-economic gains by way of base oil yield and quality benefits.

The long experience of the R&D group comprising high experienced scientists engaged in these studies at

IIP has resulted in the completion of 55 technological studies.

### **Testing facility for plastics**

Plastics are being used for packaging foods in various forms. These plastics in finished form contain additives like plasticizers, stabilizers, antioxidants, colorants, etc. Also, they carry inherent polymerization residues like monomers, catalysts, etc. in trace quantities. These are likely to migrate into food and pose health problems in view of their toxic nature. With increased common awareness on health and environmental pollution posed by indiscriminate use of plastics, more and more stringent regulations are being imposed for food packaging materials all over the world. Proper testing and evaluation of plastics by suitable testing procedures is of great national importance and ensures safety of use of these materials.

In this context, the Central Food Technological Research Institute (CFTRI), Mysore, has built up, over the years, excellent facilities to test plastic containers for their safe use for packing food and oils and fats. So far, the Institute has tested more than 1000 plastic materials at the request of manufacturing and user industries. Full-fledged facilities are also being set up to estimate monomers like vinyl chloride, a carcinogenic compound present in PVC containers in minute (ppm level) quantities.

### **Small-scale mining**

With its vast experience, ample expertise and modern infrastructural facilities CMRS, the leading mining R&D institute in the country, has set up a consultancy cell for small-scale mining to provide adequate technical consultancy to small-scale mining industry on the following aspects at concessional rates: (i) Assessment of techno-economic feasibility of new mining projects, (ii) Detail mine planning & design, (iii) Environmental impact assessment, (iv) Operational problems, (v) Improvements of techno-economics in existing mines, (vi) Human resource development, and (vii) Quality control.

The small mines in India can now avail the benefits of the modern scientific means to sort out their long-term as well as day-to-day problems in a



techno-economically viable, environment-friendly and sustainable way.

#### **Ultra-high vacuum scanning tunneling microscope**

An ultra-high vacuum scanning tunneling microscope (UHV-STM) has been developed under the United States India Fund (USIF) programme as a successful collaborative effort by Central Scientific Instruments Organisation (CSIO), Chandigarh; M/s Vico, New Delhi, and Naval Research Laboratory (NRL), Washington.

STMs both for use under ambient condition and ultra-high vacuum developed under USIF are being jointly used by CSIO, IMTECH-Chandigarh, CCMB-Hyderabad, and other laboratories for imaging variety of samples.

#### **Technology for export of mango**

The Central Food Technological Research Institute (CFTRI), Mysore, has standardized a package of pre- and post-harvest technologies for commercial scale of (10 to 60 tonnes per day) handling of *Alphonso* and *Banganapalli* variety mangoes for their export by ship in reefer containers, at a far reduced freight charges and thus paved the way to boost India's share in the world market. The technology is first of its kind in the country. The freight charges for export of mangoes by ship are almost 60 per cent cheaper than the prevailing air-cargo charges enabling the exporters to earn substantial profits.

Apart from considerable reduction in freight, the

package allows export of mangoes in bulk quantities to distant foreign markets, extension of storage life of mangoes by over 30 days and facility to ship quality fruits with desired ripening characteristics at the destination.

The CFTRI technology was successfully adopted in 1992 itself by an export firm in Gujarat for shipment of seven tonnes mature *Alphonso* mangoes each to Germany and England. Again, Maharashtra State Agricultural Marketing Board, Pune exported 140 tonnes of *Alphonso* mangoes in eight reefer containers by ship to Gulf countries and England in the last season. Further, CFTRI's pre- and post-harvest technology package was used for exporting of *Banganapalli* mangoes by ship to Hongkong.

The technology package includes orchard management, pre-harvest treatments to control fungal and insect damages; optimum stage of maturity for harvest, desapping, handling, transportation; packing house operation such as grading, washing; post-harvest treatments to minimize fungal spoilage; packing in specially designed corrugated fibre board boxes; unitizing and palletizing, pre-cooling, stacking in refrigerated containers, optimizing low temperature and humidity conditions and post-transportation ripening conditions.

The CFTRI's technology and expertise for exporting mangoes can be availed by any interested firm/agency. More details can be obtained from Director, CFTRI, Mysore 570013.



## R&D Meetings

### Microtronica India '94

India's second exhibition and conference on electronics production equipment, testers, materials, operating supplies, components and technologies will be held during 19-22 October 1994 at Ashok Hotel, Bangalore. It is being organised by CONVEX (Conventions & Expositions) in cooperation with the Indian Chapter of the International Society for Hybrid Micro Electronics (ISHM).

The exhibition focuses on equipment, material and operating supplies for electronics production and testing including printed circuit boards, surface mounted devices, semiconductors and integrated circuits hybrid circuits, other active and passive components for the electronics industry.

In conjunction with the exhibition a high level technical conference is planned.

Those wishing to present papers in sessions proposed for: (a) PCB/hybrid/design and fabrication, (b) surface mounting technology, (c) ASIC and IC design and manufacture, (d) component manufacturing and testing, (e) electronic materials and chemicals are advised to send 500 word abstracts to the organisers by July 15th, 1994.

Contact address:

Conventions and Expositions

A Division of Applied Technology Services Pvt Ltd  
14F, Basant Lok, Vasant Vihar, New Delhi 110 057

Tel: 670346, 675671 Telex: 031-82031

Fax: 91-11 6875598, 91-11-6893081

P-239, 9th Main, Sector 10, Jeevan Beema Nagar  
HAL-III, Bangalore 560 075

Tel: 080-5581806, Fax: 080-5581806

### Autofact '94 Conference and Exposition

5-day conference: November 13-17, 1994

3-day exposition: November 15-17, 1994

Cobo Convention Center

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The Society of Manufacturing Engineers and the  
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Contact:

Kristy Harrington

SME Market Planning and Communications

Phone: 313/271-1500, ext. 433

### Electronics India '94

The 4th International Electronics and Telecommunications Exhibition will be held during 7-11 September 1994 at Pragati Maidan, New Delhi. It is expected to open fresh avenues for technologies and services related to:

1. Multimedia and computing systems
2. Software, peripherals and consumables
3. Office automation equipment systems
4. Testing/measuring instruments
5. Process control systems
6. IT-based flexible manufacturing
7. Systems and CAD/CAM systems
8. Telematics and networks
9. Consumer electronics
10. Electronic components devices, and microprocessors
11. Telecommunication and broadcasting
12. Industrial and medical electronics, and
13. Capital goods.

More information can be had from:

The General Manager

Domestic Fairs Division

India Trade Promotion Organisation

Pragati Bhawan, Pragati Maidan

New Delhi 110 001

Telex: 031-61311, 61022

Fax: 011-331-8142

Gram: COMEXH

### International symposium on production and application of lube-base stocks

The Indian Institute of Petroleum (IIP), Dehra Dun, in collaboration with the Centre for High Technology, Engineers India Ltd, Hindustan Petroleum Corporation Ltd, Indian Additives Ltd, Indian Oil Corporation Ltd, Indo-Burma Petroleum Co., Lubrizol India Ltd and Madras Refineries Ltd, is organizing an international symposium on production and application of lube base stocks at IIP, Dehra Dun, during 23-25 November 1994.

The topics of the symposium are: Technological



advances in production of lube oil base stocks, Determination of compositional parameters of base stocks, their significance in processing and lubricant performance, Base stock properties/characteristics, Additive response and their inter-relationship, Synthetic and environmental-friendly base fluids for lubricants and Lubricant blending technology.

For further information contact: Dr Himmat Singh, Organizing Secretary, International Symposium on 'Production and Application of Lube Base Stocks', IIP, P.O. IIP, Dehra Dun 248 005.

#### **Research-industry meet on wear-resistant ceramics**

Sometime back a research-industry meet on wear-resistant ceramics was held at the Central Glass & Ceramic Research Institute (CGCRI), Calcutta. The CGCRI scientists had worked hard to build up the technology for wear-resistant ceramics—to give it the shape of a complete technology package. The appreciative report received from Hindustan Aeronautics Ltd (HAL) on performance of this technology in enhancing successfully the service life of jet aeroengine components played a positive role towards its transfer to some other private and public sectors industries. And, negotiations with several industrial firms are going on for commercialization of the technology. The most important point to be noted is that there is a vast scope for application of this technology in different type of industries, starting from aeronautics to food, breweries to automobiles, thermal power plants to textiles and many other which can be benefitted by the use of this technology.

#### **APCTT-CSIR-NSIC technology transfer consortium**

The Asia-Pacific Centre for Technology Transfer (APCTT) with a wide network of technology transfer

consultants spread over 70 countries, the Council of Scientific and Industrial Research (CSIR) with a tank full of over 2000 technologies suitable for small scale sector, and the National Small Industries Corporation (NSIC), the godfather of small industries, have teamed up to form a consortium which will help small scale industrial units to choose and upgrade technologies, productivity, improve design standards, and raise efficiency to make themselves competitive in the world trade which has been thrown open to all. The SSI account for fifty percent of total manufacturing in value addition terms and 42 percent of exports. In order to expose the SSI units to the national and international technological developments of relevance to them and to evolve suitable mechanisms and appropriate follow up action with technology-oriented units, the consortium is organising a number of workshops at major SSI clusters.

The first of these workshops was held at New Delhi on 4th and 5th July 1994. While inaugurating the workshop Mr M. Arunachalam, Union Minister of State for Industry, announced that the Capital's first software technology park will become operational at the Okhla Industrial Estate in the near future. Once operational the park will provide ample opportunities and access to fast communication linkages for transmitting data to software professionals. It would also give the necessary push to export of software from the country. Referring to the government's efforts to streamline the functioning of the small sector and ensure the availability of all inputs, especially finance on favourable terms, Mr Arunachalam said a separate bank—Small Industries Development of India (SIDBI)—had been set up. The government, he said, had released Rs one crore to SIDBI for development of four integrated infrastructural development centres.



## Technical Literature

**R&D Strategies in Japan—The National, Regional and Corporate Approach** by H Eto (Elsevier Science Publishers, BV, Amsterdam, The Netherlands), 1993, pp. 314, Price: Dfl 250.00; US \$ 142.75.

According to the editor, the book has three purposes: (i) to shed light on how innovations and R&D are conducted and promoted or prevented by national or local governments and enterprises; (ii) to provide clues to understand the implications behind the descriptions in view of the singularity and universality of the so called Japanese management; and (iii) to clarify the universality of R&D activities.

The entire book is an amalgamation of 12 chapters divided into three parts.

Part 1 consists of four chapters on R&D management by new approaches. Chapters 1 and 2 are based on experiences of the authors. Chapter 1 by Takahashi reports on how new QC (Quality Control) tool has been useful to get higher productivity in Japanese companies. The chapter is a case study of the R&D management in 'Sumitomo Metal Mining', an oldest Japanese enterprise. This also overviews the post oil crisis development of corporate strategies of R&D in Japan.

Chapter 2 by Odajima also deals with the application of the QC approach to new product development in a chemical firm. Both these chapters devoted to management appear to be written for R&D personnel well acquainted with QC techniques as the section dealing with the application of these techniques is brief and the bibliography provided at the end is also very brief.

Chapter 3 on 'R&D Strategic Policy of Local Government' by Iwasawa *et al.* discusses role of science and technology (S&T) strategic policies in general and research and development (R&D) strategic policies, in particular, in local governments through a case study of Kanagawa Prefecture.

In Chapter 4, Kobayashi tries to explain the social and cultural background of the drift of the young people away from S&T. The essay supports Ortega's hypotheses that when technology develops to its maximum, by contrast situations emerge in which the number of young people engaged in scientific and technological pursuits will decrease, which results 'Savages in a Civilized Society' whose receptivity towards the fruit of science and technology is high,

but who do not have any interest in the process of S&T.

Second part of the book comprises of five chapters on various aspects of evaluation of R&D activities. The chapters on 'R&D and auditing in the public sector' describes how the Board of Audit, a government auditing authority, has been implementing financial control over public sector R&D consistent with researchers autonomy.

Chapter 6 by Bjorn on 'Japanese Articles on Research and Development Published in International Journals, depicts the poverty of Japan's scientific activities in the field of R&D management, although Japanese companies have made great impact on the world during the last 20 years, but the impact of articles by these companies on R&D is much smaller than the articles written by authors affiliated with universities or governmental institutions.

Significant inter-firm and inter-regional differences in product development performance such as lead time, development productivity, and total product quality has been presented in Chapter 7 by Fujimoto. The chapter is a case study of the auto industry, which is most important sector of Japan facing a trade conflict with the USA.

In Chapter 8 Yamamoto emphasises for improvements of the research environment at universities in order to strengthen basic research at universities and maintain the competitiveness of Japan.

Saito earlier a researcher and now a manager in an industrial research organization has proposed a two layered R&D model discarding the traditional linear R&D model, which is inadequate to describe recent dynamic R&D activities and the two-layered R&D model proposed here adequately describes their characters by relating R&D to STOCK and FLOW.

Part 3 consisting of three chapters on the *status-quo* of R&D of Japan in the past, present, and in the future. The first chapter by Niwa and Colo in this part is the survey of collaborative R&D of Japanese companies to clarify its strategy, future trends, and components of successful R&D management. The results indicate that in the past, the main target of collaborative R&D seems to have been economizing R&D resources. While at present it is reinforcing



technological potential based on synergy effects. In the future stress will be more on social contributions as well as international R&D collaborations.

In the second chapter of this part, Eto presents historical review of S&T policies, from which many possible obstacles for the future development of R&D are identified.

The last chapter for this part by Phillips discusses about the effect of Japanese attitude and behaviour in carrying basic research and how these attitudes and behaviour patterns tend to promote or discourage the success of creative research effort.

Of the 12 chapters discussed in the book, some of the chapters fit in well within the scope of the title and purpose of the book, while a few others deal indirectly with R&D strategy. The book on the whole presents a lucid picture of R&D strategy in Japan *vis-a-vis* of Japanese culture and education.

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**Research and Development in Indian Industry** by G C Beri (Concept Publishing Co., New Delhi 110059), 1993, pp. 128; Price (not given).

Though R&D is central to economic development, so far in India, like many other developing countries, it has not received adequate attention. However, there is now increasing realisation that something ought to be done to promote R&D. The book under review is on this subject of growing importance.

The book contains in all nine chapters. The first chapter deals with some conceptual aspects and describes the main approach adopted by the researcher. It also highlights that R&D is a relatively recent phenomenon in India.

Chapter 2 first deals with concept and the process of technological change. This is followed by a discussion on the relationship between technological change and the economic performance at the firm's level.

Chapter 3 deals with major trends in R&D activity in India. It gives a comprehensive analysis covering such aspects as R&D expenditure by sectors, R&D expenditure by major scientific agencies, R&D expenditure in selected industries, R&D intensity in public and private sectors, international comparisons of R&D expenditure, growth of patents in India and R&D output by sectors in India.

The study indicates that industrial R&D in the private sector is at a very low level accounting for only 23 per cent of the total R&D expenditure. Public

sector units having more financial resources comparatively spending more in R&D. Among the industries, the most significant increase in R&D expenditure was in fuels. In contrast, there was a marked decline in chemicals. A distressing feature is that on the whole R&D intensity is extremely low in Indian industries. There are very large differences between R&D expenditure in the small scale units and that in medium and large scale units. Although R&D expenditure by cooperative research associations is on the increase, it still constitutes mere 0.43 per cent of the total R&D expenditure.

An analysis on the patents suggests that innovations are very negligible in India. This perhaps also shows that largely R&D activity in India is in regard to adapting imported technology which obviously does not lead to innovations.

Chapter 4 focuses on R&D at the micro level. It describes R&D practices in selected enterprises belonging to different industry groups. At the end, an approach to generalisation has been made by identifying some major factors that have contributed to the successful R&D in selected enterprises.

To know at first hand what R&D managers feel about R&D activity in their enterprises, an opinion survey was made, Chapter 5 analyses the survey data. The main hurdles faced by R&D managers have been brought out. In addition, some useful suggestions made by them for strengthening R&D activity are specified.

The author has pointed out that one of the weakest areas of R&D is the lack of institutional collaborations. Chapter 6 deals with institutional collaborations in R&D activity. It discusses collaboration between IITs and industry. This is followed by a discussion on collaboration between university and industry. Towards the end, the chapter gives a detailed account of NRDC and makes certain suggestion so that the NRDC can play a more effective role than hitherto in promoting R&D in India.

Chapter 7 is devoted to the government policy relating to R&D. The following conclusion seem to emerge from this discussion: First, the government has to play a crucial role in the upgrading of technology. It has become imperative to integrate technology policy with industrial policy.

Chapter 8 focuses on R&D statistics in India. Major limitation of R&D statistics especially in regard to R&D expenditure are pointed out. In addition, it makes a number of suggestions for improving and enlarging the scope of such statistics.

Finally, Chapter 9 brings out the major conclusions emerging from this study. Some of the



conclusions are in the form of specific suggestions covering a wide area.

The book is appended with: (i) the questionnaire circulated for the opinion survey, (ii) list of incentives available to R&D units, (iii) an exhaustive bibliography on the topic, and (iv) an index.

In the context of changing business environment in India, as a consequence of shift in the government's industrial policy, the findings of this study assume considerable importance.

**Small-Scale Manufacturing Industries in India: Some Aspects of Size, Growth and Structure** by K V Ramaswamy (Indira Gandhi Institute of Development Research, Goregaon (East), Bombay 400065), 1994, pp. 35.

This is short report organised in five sections. Section briefly describes the data sources for different segments of manufacturing of the study. Analysis of changes in the structure of manufacturer employment is given Section 2. The Section 3 is the major section discussing size, growth and structure of employment value added, reserved products and exports of the small sector. In the 4th section, a comparison of wages and productivity in the small sector with the large sector is given. The manufacturing sector has been divided into two segments, household and non-household. The former is run by head of the household himself at home and the other is the registered sector under the Factory Act of 1948.

The main findings of the report are summarised as follows:

The decade of the eighties is characterized by the changing structure of manufacturing employment. Non-household employment has risen while household employment has continued to decline. A significant finding is the rise in the share of non-factory segment, between 1981 and 1991, from 56 percent to 65 percent and the decline of the factory sector from 44 percent to 35 percent, within the non-household sector. The estimates suggested that most of the addition, if not the entire, has come from non-factory non-household segment. The non-factory non-household segment of manufacturing has been regarded as the small-scale industry. This partly reflects a shift from factory to small-scale industry, a type of structural change not explicitly recognized by the received stylized explanations of the size structure of manufacturing.

The SSI sector, covered by the Second Census of such units (1987-88), is found to be a small segment of the manufacturing sector. It's estimated share in total manufacturing employment and value added is

found to be 12 percent and 20 percent respectively. The SSI units have recorded impressive growth rates of employment and value added across industry groups. Increase in the estimated labour productivity is found to be significant over the period 1972 to 1987-88. Estimate of aggregate capital productivity showed a marginal decline. From this it has been conjectured that the resources use efficiency, in the aggregate, has not declined in the SSI sector. Wages and labour productivity are found to be positively related. Export intensity of the SSI sector is found to be comparable to that of the private corporate sector.

The structure of the SSI sector has not undergone any substantial change over the period 1972 to 1987-88. Broadly speaking, the primary material and agro-based industries namely, food products, beverages and tobacco products, wood, leather, paper products and hosiery and garments have shown a tendency to improve their employment and value added shares relative to metal based industries. Their better economic performance perhaps is largely due to the industry specific characteristics rather than to governmental protection as noted the metal based industries have a larger share of reserved products. This suggests that industry characteristics are more important determinants of small-scale enterprise growth.

The estimated output share of reserved items in industries with larger share of number of reserved items has not increased. This implied that the production of reserved items is not a dominant production activity of SSI units. Only 48 of the 843 reserved items figured in the list of 200 leading SSI products. This seriously questions the continuing policy of reservation for exclusive SSI manufacturing.

In 1987-88, on the basis of employment shares, seven industries are found to be small establishment oriented, namely, wood products, hosiery and garments, non-metallic mineral products, metal products, tea, leather products, rubber and plastic products and food products.

Finally, it has been observed that in 1987-88, wages are lower relative to the large scale sector but labour productivity is not proportionately lower. This may be interpreted as providing some support to the hypothesis that shift to non-factory is due to labour cost advantages of small-scale production.

**New projects for Small Entrepreneurs** (Food Products), (Development Commissioner, Small Scale Industries, Department of SSI & ARI, Ministry of Industry, Govt of India, Nirman Bhawan, New



Delhi 110001), 1st edn, Vol. II (1994), pp. 159, Price: 47.00, £ 1.26, \$ 1.78.

This is the second volume of New Projects for Small Enterprises brought out by the Department of SSI & ARI, Govt. of India. The volume contains 39 project profiles on food products that can be taken up for production by small entrepreneurs. The profiles carry market information, method of manufacture, machinery and raw materials required, quality control, capital inputs, production cost and

profitability. All this is very essential information for any new entrepreneurs. The information has back up support of over sixty small industry service institutes and centres. The topics discussed include: honey processing, bakery items, canned mushrooms, coconut/cashew feni, dal milling, dry ginger, frozen fish, fruit nectar, spices, ice plant, hatchery, mango kernel oil, noodles, papad, potato wafers, pineapple processing, prawns/shrimps farming squashes, vinegar and others.



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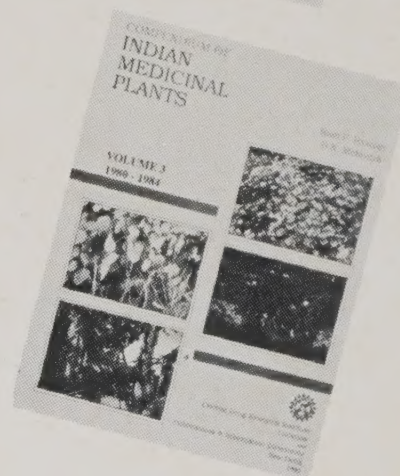
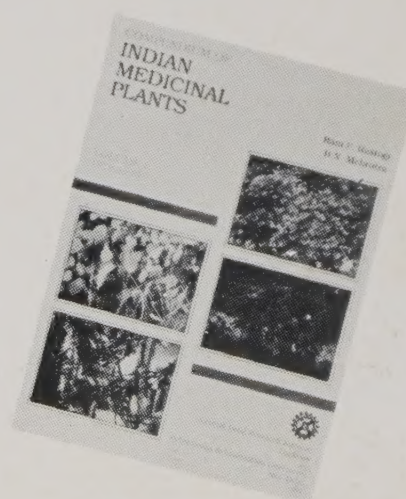
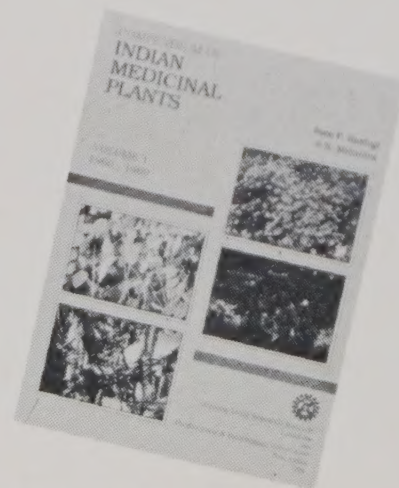
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